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THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*Frangulin.* PART II.

By T. E. THORPE, F.R.S., and A. K. MILLER, Ph.D.

IN a previous communication, one of us, in conjunction with Mr. H. H. Robinson (Trans., 1890, **55**, 38), gave the results of an investigation undertaken with the view of clearing up the discrepancies in the statements of previous experimenters with regard to the composition of frangulin and the nature of the products of its hydrolysis. These results were not so complete as we could have desired, owing to lack of material. The question, however, has been again attacked, and we now bring before the Society the completion of our work on this subject.

Preparation of Frangulin.

In order to prepare sufficient frangulin for our purpose, we obtained 2 cwt. of the bark of the alder buckthorn, *Rhamnus frangula*, and entrusted the preliminary work of extraction to Mr. John Moss, Galen Works, Deptford, to whom our best thanks are due.

The bark was crushed and treated in a percolator with low boiling petroleum to remove fat and chlorophyll. A portion of the percolated bark was subsequently digested with ether, but the loss of ether by evaporation was so great that the use of this liquid was abandoned, especially as the extracts thus obtained did not readily yield frangulin. The rest of the bark was therefore exhausted by percolation with methylated spirit, and the extracts were obtained partly in the form of a thick, black, tar-like fluid, and partly as a thin, black liquid. This portion of the work was carried out at Mr. Moss's works.

The method which we first adopted in order to obtain the frangulin from these extracts was essentially that described in the paper already referred to. The extract was mixed with three or four times its volume of hot methylated spirit, and allowed to settle, when little spheres of crude frangulin sank to the bottom of the vessel, and could be readily separated. The liquid, which still contained the bulk of the frangulin, was then treated with lead acetate to throw down the tannin, and hydrogen sulphide was passed through the filtrate to remove the excess of lead. The filtrate from the lead sulphide was concentrated at as low a temperature as possible, under greatly reduced pressure, in order to minimise the hydrolysing action of the acetic acid liberated by the hydrogen sulphide. This concentrated liquid was set aside for several days, during which time it deposited crystals of sulphur and a certain amount of crude frangulin. These were separated by filtration, and the liquid was then evaporated to dryness with the addition of barium sulphate or sand; the residue was coarsely powdered and sifted, and extracted with ether in the apparatus which had been previously used for this purpose.

Owing to the large bulk of extract to be treated, this process proved to be extremely slow and tedious. After a few trials it was found that the precipitation of the tannin might be omitted, and the simplification thus introduced not only effected a considerable saving of time, but it also diminished the risk of the frangulin becoming partially hydrolysed during the process. The bark extract was merely evaporated to dryness with sand or barium sulphate, and the powdered product exhausted with ether, as in the first case. The ether was distilled off from the extracts, and a little alcohol added to the dark-coloured residue; the greater part of the frangulin separated after standing for a few hours, and more was obtained on allowing the filtrate to remain for several days, or even weeks.

In order to purify the crude frangulin, it was introduced into a capacious flask, and fractionally extracted with boiling methylated spirit. The first extracts were the most impure; they were deeply coloured, and contained *emodin*, which is comparatively easily separated from the frangulin, on account of its ready solubility in hot spirit. The last extracts, on the other hand, contained some foreign substance which is but sparingly soluble in alcohol, and hence it became very difficult to separate it completely from the frangulin. These extracts deposited the frangulin as a yellow, amorphous powder, destitute of the lustre which is so characteristic of the pure substance. The intermediate fractions, on cooling, yielded distinctly crystalline frangulin with a decided lustre; this is best purified by several recrystallisations from boiling alcohol. As the solution of the purified product cools, the frangulin separates in a microcrystalline condition, exhibiting a magnificent golden, satiny lustre, which is best seen on gently agitating the flask. It appears to be useless to attempt to carry the purification beyond a certain point, as even boiling alcohol hydrolyses frangulin to a perceptible extent, and the product thus becomes mixed with emodin. Schwabe recommends glacial acetic acid as the medium for crystallising it from, but on trial we found that it hydrolysed the frangulin much more readily than alcohol. Other solvents, such as acetone, benzene, ethyl acetate, and chloroform were also tried, but frangulin is so sparingly soluble in all that they are of comparatively little value.

Composition.

In the first paper a number of concordant analyses were given, the results of which seemed to indicate that frangulin had the composition $C_{22}H_{22}O_9$. At the same time it was pointed out that the amount of emodin obtained on hydrolysing weighed quantities of frangulin was in excess of that required by this formula, and that it was more in accordance with the formula $C_{21}H_{20}O_9$. The quantity of frangulin at that time obtained was, however, too small to enable us to identify the second product of hydrolysis, and we were led to give greater weight to the analytical numbers than to the result of the hydrolysis experiments. Hence it was concluded that frangulin had the composition indicated by the first of the above formulæ.

After repeating and extending these experiments with the larger quantity of material which we have now been enabled to prepare, we have come to the conclusion that, owing to the great difficulty of preparing absolutely pure frangulin, it is scarcely possible to determine its composition with certainty by analysis alone, for although it is easy to prepare a distinctly crystalline and apparently pure product, we have been unable to obtain any definite test by which its purity can be proved. In order to establish the composition of frangulin, it is necessary that the composition of both the products of its hydrolysis should be known, as well as the percentage yield of at least one of these products, and, further, that these data shall be reconcilable with the empirical formula of frangulin deduced from its analysis.

We have now satisfactorily determined the necessary data, and from the results which we have obtained we conclude that frangulin has the composition indicated by the formula $C_{21}H_{20}O_9$, which is that previously assigned to it by Schwabe (*Arch. Pharm*, 1888, **226**, 569).

The following are the results of a fresh series of analyses; for comparison, we append the mean of the earlier results:—

I. 0·1902 gram of air-dried frangulin lost 0·0044 gram of water when dried at 120°.
II. 0·4971 gram of frangulin lost 0·0116 gram of water when dried at 120°.
III. 0·4261 gram of frangulin lost 0·0087 gram of water when dried at 120°.
IV. 0·9007 gram of frangulin lost 0·0205 gram of water when dried at 120°.

Found.					Calculated for
I.	II.	III.	IV.	Mean.	$C_{21}H_{20}O_9 + \frac{1}{2}H_2O$.
2·31	2·33	2·04	2·27	2·24	2·12 per cent. H_2O.

I. 0·1858 gram of frangulin, dried at 120°, yielded on combustion 0·4133 gram of CO_2 and 0·0859 gram of H_2O.
II. 0·2054 gram of dried frangulin gave 0·4590 gram of CO_2 and 0·0989 gram of H_2O.
III. 0·1957 gram of dried frangulin gave 0·4360 gram of CO_2 and 0·0936 gram of H_2O.

	Found.				Mean of
	I.	II.	III.	Mean.	former results.
C	60·66	60·94	60·75	60·78	61·20 per cent.
H	5·13	5·35	5·31	5·26	5·29 ,,

	Calculated for.	
	$C_{21}H_{20}O_9$.	$C_{22}H_{22}O_9$.
C	60·57	61·40
H	4·80	5·11

It will be seen that although our new analyses do not differ greatly from those given in the former paper, they agree much better with the formula $C_{21}H_{20}O_9$ than with $C_{22}H_{22}O_9$, although the numbers for both carbon and hydrogen are somewhat high. We believe that the explanation of this is that our frangulin contains a small quantity of a new substance which we have succeeded in isolating, and found to be isomeric with emodin. It differs from the latter, however, in being but sparingly soluble in alcohol, and is on this account difficult to completely separate from the frangulin.

For the definite proof of the composition of frangulin, we depend, however, mainly on the results of our hydrolysis experiments.

Hydrolysis of Frangulin.

The hydrolysis of frangulin is most conveniently effected by boiling it with aqueous alcohol containing about 2 per cent. of sulphuric or hydrochloric acid, preferably the latter. The following are the proportions which we have found to answer best:—1 gram of frangulin is boiled for some hours with a mixture of 35 c.c. pure alcohol, 15 c.c. water, and 3 c.c. concentrated hydrochloric acid, or a corresponding quantity of sulphuric acid. As hydrolysis proceeds, the frangulin gradually disappears, and a clear, reddish-brown solution is finally obtained. At this stage, the hydrolysis is probably complete, but in order to make quite sure, the heating is continued for another hour. The product is then transferred to a dish, a little water is added, the alcohol is driven off by heat, and more water added from time to time in quantity rather more than sufficient to replace the alcohol and water lost by evaporation. In this way the whole of the insoluble product separates in a crystalline state, and is best collected by filtration through a weighed Gooch crucible. The product is then dried at 125—130° until constant in weight.

The following results were obtained:—

I. 0·5667 gram of frangulin, dried at 120°, yielded 0·3732 gram product (emodin) insoluble in water.

II. 2·4482 grams of dried frangulin yielded 1·6288 grams of product insoluble in water.

	Found.			Calculated for	
	I.	II.	Mean.	$C_{21}H_{20}O_9$.	$C_{22}H_{22}O_9$.
Yield of insoluble product (emodin)	65·9	66·5	66·2	64·9	62·8

In calculating the theoretical yield for the above two formulæ we have assumed that emodin has the composition $C_{15}H_{10}O_5$. This was shown to be the case in the first paper, and the experiments therein recorded confirmed the results previously obtained by Liebermann and Waldstein (*Ber.*, 1876, **9**, 1775), and also by Schwabe (*loc. cit.*).

It will be seen that the yield of emodin agrees closely with that (67·6 per cent.) found in the earlier experiments, and is almost identical with that (66·0 per cent.) given by Schwabe. For an experiment of this class it is also a close approximation to the requirements of the formula $C_{21}H_{20}O_9$. The fact that the percentage of emodin found is somewhat higher than that demanded by theory is easily explained on the assumption that the frangulin contained a little of the impurity alluded to; this would necessarily be collected with the emodin, and thus add to its weight.

In the hope of discovering some clue to the nature of the substance which so persistently clings to the frangulin, we made some experiments with one of the most sparingly soluble fractions obtained during the purification of the frangulin, as above described. This crude product was free from the satiny lustre which characterises the pure substance, and it was evident that the impurity which it clearly contained must be very sparingly soluble in alcohol. On hydrolysing this crude frangulin, it was noticed that a yellow residue remained undissolved. This was at first thought to be unchanged frangulin, but as it did not appear to undergo any further change, it was filtered off and boiled with a fresh quantity of dilute acid in alcoholic solution. It was then found that the substance did not hydrolyse, and was, therefore, not frangulin. It dissolved sparingly in boiling alcohol, and after a few recrystallisations from the latter, was readily obtained in golden-yellow needles melting constantly at 202—203°. This was evidently the substance discovered also by Schwabe, and which he found to melt at 199°. Schwabe was apparently unable to determine its composition, but he states that it seems to be related to emodin. We find that it has, in fact, the same composition as emodin, and it is, in all probability, an isomeric trihydroxymethylanthraquinone. If differs from emodin in colour, in melting point (emodin melts above 250°), and in the fact that it can be much more readily sublimed. It dissolves in concentrated sulphuric acid, forming a red solution, which is somewhat bluer in shade than that yielded by emodin. Unlike the latter, it is almost insoluble in cold ammonia, is sparingly soluble in hot ammonia, is nearly insoluble in moderately strong caustic soda or potash, but dissolves in dilute solutions of potash or soda with a red colour. Emodin, on the other hand, dissolves readily with a deep-red coloration, in either dilute or concentrated solutions of ammonia or the fixed alkalis.

0·1649 gram of the substance lost no water when heated at 120°, and yielded, on combustion, 0·4042 gram of CO_2 and 0·0641 gram of H_2O.

	Found.	Calculated for $C_{15}H_{10}O_5$.
C	66·85 per cent.	66·67 per cent.
H	4·32 ,,	3·70 ,,

Product of Hydrolysis Soluble in Water.

The filtrate from the emodin, which contained a small percentage of hydrochloric acid, was neutralised with silver carbonate, care being taken to avoid any great excess of the latter, as it appears to act as an oxidising agent when in contact with the neutral solution. A trace of silver is, however, always found in the filtrate from the silver chloride, and when the solution is concentrated a separation of metallic silver occurs. This is removed by filtration, and the solution further concentrated to the consistence of a *thin* syrup. When this is set aside in an open vessel, so that further evaporation may take place slowly at the ordinary or a very slightly higher temperature, crystallisation soon sets in, and after a short time the product becomes a solid mass of crystals. If, however, the concentration be carried too far, a *thick* syrup is obtained, which will not crystallise. The crystalline product was washed with a little methyl alcohol, and recrystallised from water.

In our first experiments we failed to obtain the sugar in a crystalline state, and this was, no doubt, mainly due to the fact that we employed sulphuric acid in aqueous alcohol for the hydrolysis of the frangulin. Although the alcohol was considerably diluted, and only a small percentage of sulphuric acid was employed, a little ethyl hydrogen sulphate was produced. After neutralising the product with barium carbonate, and evaporating the filtrate to a small bulk, a syrup was obtained, containing the sugar, together with barium ethyl sulphate; on account of the ready solubility of the latter, its complete removal could not be effected, and its presence no doubt interfered with the crystallisation of the sugar.

Schwabe employed aqueous sulphuric acid containing 20 per cent. of the latter. We have also tried aqueous sulphuric acid for the hydrolysis, and although it gives satisfactory results with a soluble glucoside such as quercitrin, we do not recommend it for quantitative experiments with frangulin. As both frangulin and emodin are practically insoluble in dilute aqueous acid, the hydrolysis is necessarily much slower and its completion much more uncertain than when a solvent is used. In an experiment which we made with 2 per cent. aqueous sulphuric acid, we found that the hydrolysis was incomplete after several hours boiling, but that the small quantity of sugar which was produced could readily be made to crystallise.

In the experiments with alcoholic hydrochloric acid, we succeeded in one case in obtaining a crystalline sugar from 1 gram of frangulin, and in a second case we obtained a similar result from 3 grams of frangulin.

Although Schwabe did not obtain sufficient sugar to enable him to determine its composition, he found that it readily reduced Fehling's solution, that it was dextrorotatory, and that it did not ferment with yeast; and from these properties he concluded that the sugar was in all probability rhamnose.

In order to make a direct comparison between frangulin sugar and rhamnose, we prepared some rhamnose from quercitrin, and from the results obtained from this comparison, as well as from our analytical numbers, we are able to confirm the correctness of Schwabe's conclusion.

We find that,—

1. The *crude* sugar from both sources fermented with yeast, though not so readily as dextrose.

2. The *crystallised* sugar from both sources did not yield a trace of gas when well-washed, active yeast was added to its solution.

Liebermann and Hörmann (*Annalen*, **196**, 335) likewise found that crude rhamnose from xanthorhamnin fermented with yeast, whilst the purified product did not ferment.

3. The pure sugar from frangulin melted at 95—96°. Liebermann and Hörmann state that rhamnose melts at 92—93°, but that differences of several degrees occur on varying the conditions under which the melting point is determined. A direct comparison showed that rhamnose and frangulin sugar melted simultaneously at 95—96°.

4. The osazone obtained on heating the solution of frangulin sugar with phenylhydrazine hydrochloride and sodium acetate was identical in appearance with the osazone prepared from rhamnose, and both melted at 180°; this is also the melting point given by Fischer (*Ber.*, **20**, 1091) for the osazone of rhamnose.

5. Frangulin sugar, like rhamnose, is dextrorotatory. As the rotatory power of this sugar is low and the amount which we were able to prepare was very small, we have not been able to determine the degree of rotation.

6. Frangulin sugar also resembles rhamnose in having a sweetish taste and in readily reducing Fehling's solution.

7. The analytical numbers obtained from frangulin sugar and from its osazone also prove that in composition it is identical with rhamnose.

0·2190 gram of the air-dried sugar lost 0·0226 gram of water when dried at 105—110° and gave on combustion 0·3111 gram of CO_2, 0·1309 gram of H_2O, and 0·0011 gram of ash.

	Found.	Calculated for $C_6H_{12}O_5 + H_2O$.
Water of crystallisation...	10·32	9·89 per cent.

	Found.	Calculated for. $C_6H_{12}O_5$.	$C_6H_{12}O_6$.	$C_7H_{14}O_5$.
C......	43·44	43·90	40·00	47·19
H......	7·44	7·31	6·67	7·86

The fact that our sugar yielded a trace of ash showed that it was not absolutely pure, but as the quantity of recrystallised product amounted only to 0·4 gram, further purification was not possible, and the analysis is sufficient to show that whilst its composition agrees with that of rhamnose, it differs widely from sugars of the formula $C_6H_{12}O_6$ and $C_7H_{14}O_5$, the latter being the formula of the sugar which might be expected if the composition of frangulin were $C_{22}H_{22}O_9$.

The osazone of the sugar was purified by crystallisation from aqueous alcohol, and yielded the following results on analysis:—

I. 0·1490 gram of the substance (dried at 100°) gave on combustion 0·3459 gram of CO_2 and 0·0898 gram of H_2O.

II. 0·0850 gram of the dried substance yielded 12·2 c.c. of moist nitrogen measured at 20·2° and 768 mm. bar.

	Found.	Calculated for		
		$C_{18}H_{22}N_4O_3$, *i.e.*, osazone from rhamnose.	$C_{18}H_{22}N_4O_4$.	$C_{19}H_{24}N_4O_3$.
C....	63·31	63·15	60·33	64·41
H....	6·69	6·43	6·14	6·78
N....	16·57	16·37	15·64	15·25

Conclusions.

The results recorded above prove conclusively that the sugar obtained on hydrolysing frangulin is *rhamnose*.

It is also known that the other product of hydrolysis is *emodin*, $C_{15}H_{10}O_5$, and from the percentage yield of this, it is clear that one molecular proportion of frangulin yields one molecular proportion of emodin and consequently also one molecular proportion of rhamnose. If we add together the empirical formulæ of the two products of the hydrolysis, and from the product $C_{22}H_{22}O_{10}$ subtract the elements of water which must have been taken up during the process of hydrolysis, we arrive at the formula $C_{21}H_{20}O_9$ for frangulin, which, as we have already shown, agrees best with its percentage composition. We conclude, therefore, that there can no longer be any doubt that the formula $C_{21}H_{20}O_9$, which was first assigned to frangulin by Schwabe, is correct, and that his equation

$$C_{21}H_{20}O_9 + H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_5,$$

truly represents its hydrolysis.

II.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF EDINBURGH.

No. VI. *The Electrolysis of Potassium Acetate Solutions.*

By T. S. Murray, D.Sc.

When an aqueous solution of an acid or of a salt is electrolysed, there occurs a migration of the electropositive hydrogen or metal, as the case may be, towards the negative electrode, and of the electronegative residue, the acid radicle, in the opposite direction towards the positive electrode.

At the respective electrodes, these so-called ions give up their electric charges and become chemically free. Whatever view may be taken as to the nature of the mechanism by which the electrically charged ions find themselves at the electrodes, it remains that the part of the electrolysis of chemical import is the discharge of the ions on their reaching the electrode of opposite charge. The ions, freed from their charges, are in general incapable of existence as such; hence, subsequent chemical changes take place resulting in the formation of more stable compounds. Perhaps the simplest type of electrolytic decomposition is where the discharged ions combine with themselves to form molecules, as in the instance of the electrolysis of aqueous hydrochloric acid; here the single hydrogen atoms unite to form molecules, and similarly with the chlorine atoms. Very often, however, the accompanying chemical reactions are such as give rise to products differing entirely from the original ions. Besides being able to unite with one another, the ions may suffer decomposition into simpler compounds, or they may react on water, or on the electrolyte, or they may become oxidised or reduced, and so forth.

Examples of these differences in behaviour are to be found among many inorganic acids and salts; but it is in the electrolysis of organic acids, owing to the presence of large and, it may be, easily oxidisable groups, that the most complicated secondary reactions occur. The electrolysis of potassium acetate exemplifies this. When a very dilute aqueous solution of potassium acetate is electrolysed, the electropositive potassium ions, on being discharged at the cathode, react with the water to form caustic potash and an equivalent of hydrogen, which is evolved; and, similarly, the electronegative $CH_3 \cdot COO$ ions, or acetions, discharged at the anode, react with water with formation of acetic acid and liberation of oxygen. If we neglect the separation of potassium acetate into caustic potash and acetic acid, the products of the electrolysis are those of a decomposition of water. The reactions are expressed by equations, thus:—

$$K + HOH = KOH + H,$$
$$2CH_3{\cdot}COO + HOH = 2CH_3{\cdot}COOH + O.$$

Most acids and salts in dilute solution suffer a similar decomposition when electrolysed. Such an electrolysis, where the products are those of the decomposition of water, may be called a *Faraday electrolysis.*

If the solution of the acetate be concentrated, the reaction becomes more complicated. It was Kolbe who first sought to investigate fully the electrolysis of concentrated solutions of potassium acetate and of other similar organic salts (*Annalen*, **64**, 339; **69**, 257; *Quart. Journ. Chem. Soc.*, **2**, 157).

He found that, with a strong solution of potassium acetate, the chief reaction is as follows:—

Hydrogen is liberated at the cathode as before, but now the acetions act on one another so as to form ethane and carbonic anhydride, thus:—

$$CH_3{\cdot}COO + CH_3{\cdot}COO = C_2H_6 + 2CO_2.$$

This may be called *Kolbe's first reaction.* Simultaneously another reaction proceeds, but to a very limited extent. A small quantity of methyl acetate is formed according to the equation

$$CH_3{\cdot}COO + CH_3{\cdot}COO = CH_3{\cdot}COO{\cdot}CH_3 + CO_2.$$

This type of reaction may be called *Kolbe's second reaction.* The gas obtained on electrolysing a concentrated solution of potassium acetate possesses a peculiar ethereal odour, which Kolbe showed to be due to the presence of a vapour having properties identical with those of methyl acetate. Although the substance is present in such small quantities that it has never been isolated with certainty, yet with other acids belonging to the acetic acid series, a large proportion of the decomposition takes place according to this type of reaction; for instance, potassium valerate, on electrolysis, yields a large quantity of butyl valerate (Kolbe, *loc. cit.*).

Besides the three electrolytic reactions named—the Faraday, and Kolbe's first and second reactions—there occurs, in addition, oxidation of a portion of the electrolyte by the electrolytic oxygen.

The Faraday reaction occurs even with saturated solutions of the acetate, but the oxygen formed is never liberated as such, being entirely used up in oxidising the electrolyte, or rather perhaps, some product of the electrolysis. The formation of ethane has been explained by certain chemists (Bourgoin, Jahn, Bunge) in a way different from that given above; they regard the ethane as the result of a partial oxidation of the acetic acid by the electrolytic oxygen. This view will be discussed later.

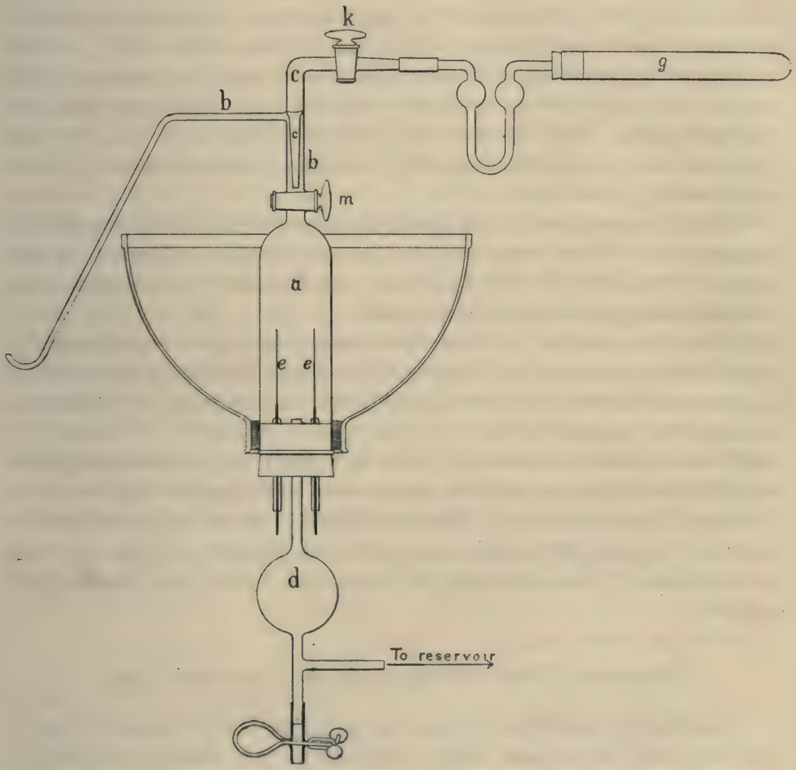
That Kolbe's reactions become more marked in strong solutions is due to the increased concentration of the acetions at the moment of their liberation. As the ions become more closely crowded together, they react to a larger extent on one another, and to a less extent on the water of solution. The concentration of the liberated ions is dependent primarily on the strength of the solution, and on the current density at the electrodes, the latter varying with the size of the electrodes and the strength of the current. The secondary reactions are also influenced by temperature, and the presence of acid or alkali in the solution likewise appears to have an effect.

At the suggestion of Professor Crum Brown, I undertook the present investigation with a view to trace the connection between the composition of the electrolytic gas and the various factors mentioned, which one would expect to influence the electrolysis.

In most of the experiments, the electrolysis of the potassium acetate was conducted in a small cylindrical vessel of about 50 c.c. capacity, provided with an india-rubber stopper. Through the stopper there passed four tubes, into two of which were sealed stout platinum wires bearing the electrodes; of the remaining two tubes, one delivered the gas, and the other was connected with a reservoir containing solution. The electrodes consisted of two pieces of stout platinum foil of equal dimensions (30 mm. × 20 mm.), distant from one another about 5 mm.

To carry out an experiment, the cell, delivery-tube, and reservoir were filled with the solution, previously boiled to expel dissolved air. The electric current was then passed, the cell being surrounded by a vessel of water at the requisite temperature, and the gases evolved were collected over mercury. On completion of the electrolysis, which lasted, as a rule, from one to three minutes, the gas remaining in the cell was driven over into the receiving tube by the solution in the reservoir. This method of expelling the residual gas was considered the most suitable. Sweeping it out by means of some inert gas would have rendered the analysis of the gaseous mixture more complicated. The current might have been allowed to pass for some time before collecting the gas; but in carrying out concentration experiments this method is objectionable owing to the change which takes place in the concentration of the solutions, especially of the more dilute ones. On the other hand, there is introduced into the method adopted an error due to the difference in solubility of the gases; it is too small, however, to affect the present results seriously. The small quantity of solution which passed over with the gas was easily removed by means of a Dittmar's absorber (gas-pipette).

N. Bunge, in a recent paper (*J. Russ. Chem. Soc.*, **21**, 538; Abstr., 1890, 1231), has warned chemists against the use in such experiments of india-rubber stoppers and connections, owing to the absorption of hydrocarbons by the india-rubber. While in the above arrangement there was little chance of any absorption of ethane taking place, seeing that the stopper was always wet with the solution, and that the experiment lasted so short a time; still, to ensure accuracy, the apparatus represented in the diagram was employed in a number of the experiments.



The cylindrical vessel *a* of about 100 c.c. capacity serves as the electrolytic cell; it is provided with a stopcock *m*, which shuts it off from the delivery tube *b*, and its lower end is closed with an india-rubber stopper bearing the platinum electrodes *e*, *e*. The tube *d* connects the cell with a reservoir containing the solution to be electrolysed. Sealed into the vertical portion of the delivery tube *b*, there is a jet *c* which reaches down as far as the stopcock. A piece of hard glass tubing *g* sealed at one end, and containing bicarbonate of soda for generating carbonic acid gas, is connected with the tube *c*. The electrolytic cell is surrounded by a vessel to contain water at any required temperature.

To perform an experiment, the cell is first filled with the solution to the level of the stopcock *m*, which is then closed. The stopcock *k* is then opened, and the tube *g* heated until all air is expelled from the delivery tube; *k* is then closed, and the current passed, and on opening *m*, the gas is driven over into the receiving tube.

Immediately all the gas has left the cylinder, *m* is closed without allowing any of the solution to pass, and the residual gas in the delivery tube is finally swept out by means of carbonic acid. In this investigation, as it was not necessary to estimate the carbonic acid evolved, it could be conveniently employed for sweeping out the residual gases. The object of the bulb at *d* is to prevent any of the gas from being carried back, during the passage of the current, by the back-flowing solution.

With this arrangement the gas does not come into contact with the india-rubber. There was, however, no appreciable difference in the results obtained by the two methods, and in most of the experiments the simpler apparatus was employed.

To find the quantity of electricity passed during an experiment, in some cases an ammeter was employed, in others the time during which the current flowed was noted, and from the amount of hydrogen evolved, the number of ampères was readily obtained. The current used throughout was obtained from a battery of accumulators with an E.M.F. of 12 volts, and the gases were analysed by the use of a Dittmar's gas apparatus. As mentioned, the carbonic anhydride evolved was not estimated, since for the purpose of the present investigation it was sufficient to determine hydrogen, ethane, and oxygen.

Presence of Ethereal Vapours in the Electrolytic Gas.

It was not intended in the present investigation to examine closely into the trace of vapour which imparts to the electrolytic gas its peculiar odour, but still it was considered advisable, before proceeding with the analyses, to devote some time to the question.

Kolbe, besides demonstrating the presence of a vapour behaving like methyl acetate, also believed that a second ethereal compound, which might probably be methyl oxide, was produced in small quantity. He found, after the removal of the oxygen by means of phosphorus and of the methyl acetate by means of strong sulphuric acid, that on exploding the residue with excess of oxygen, a smaller quantity of oxygen disappeared than theory demanded on the supposition that the mixture consisted of hydrogen and ethane. He therefore assumed the gas to contain a small quantity of methyl oxide, a substance which requires less oxygen for its combustion than ethane does, and calculated the composition of the gas accordingly. The presence of ethylene would also account for the discrepancy in his numbers, and Kolbe and Kaempf stated later that this substance was actually present (*J. pr. Chem.* [2], **4**, 46).

These two experimenters were also able to condense from the gas, by means of a freezing mixture, a liquid which they found to contain methyl acetate, methyl formate, and methyl carbonate (Kolbe and Kaempf, *ibid.*, **4**, 46). They give no details as to how these compounds were identified. Kolbe in his first experiments obtained an absorption, on exposing in the gas a coke ball soaked in strong sulphuric acid. On warming the ball after its withdrawal, the odour of acetic acid was detected. I made several attempts to condense any vapour which might be produced. The gas was passed over calcium chloride and solid caustic potash, and then through a tube surrounded by a freezing mixture; but I only succeeded in condensing a few drops of liquid of ethereal smell (Kolbe did not pass the gas over caustic potash). I also attempted to collect the vapour by passing the gas through light petroleum cooled down by a freezing mixture, and afterwards extracting the light petroleum with water. A portion of the watery extract, which had a strong ethereal smell, and which was quite neutral, was treated with 10 c.c. of decinormal hydrochloric acid, and allowed to stand in a warm place for several hours. On titrating with standard baryta water, there was found to be an increase in the acidity of the solution—

10 c.c. decinormal HCl = 9·45 c.c. baryta,
Solution + 10 c.c. „ „ = 11·46 c.c. „
2·01 c.c. excess of baryta,

equivalent to 0·013 gram of acetic acid.

This proves conclusively that there is an ethereal salt present in the gas, the increase in the acidity arising from the hydrolysis of this salt by the hydrochloric acid.

To determine whether ethylene was present or not, a solution containing 60 per cent. of potassium acetate was electrolysed, and the gas passed for about 12 hours through bromine. No ethylene bromide was obtained. This is in agreement with an experiment of Bunge's (*J. Russ. Chem. Soc.*, **21**, 557; Abstr., 1890, 1231). The gas was also passed for a long time through an ammoniacal solution of cuprous chloride without producing any precipitate. From these two experiments it would appear that no unsaturated hydrocarbons are present in the gas. Jahn (*Ann. Chim. Phys.*, **37**, 421), by distilling the residues of sodium acetate solutions which had been electrolysed, obtained a liquid which gave the iodoform test with iodine and caustic potash; he considered that this might probably indicate the presence of acetone. I also confirmed Jahn's test, but a simple trial showed that methyl acetate also gives the iodoform reaction. It was obviously this substance and not acetone which reacted in Jahn's case; to verify this, however, I passed the gas for a long time through a solution of phenylhydrazine hydrochloride and potassium acetate, and obtained no evidence of the presence of acetone. The solution of phenylhydrazine hydrochloride employed gave an immediate precipitate of the hydrazone when treated with air containing acetone vapour.

If any methyl oxide were present in the gas, a portion of it would probably be absorbed, along with the methyl acetate, by the strong sulphuric acid, in which methyl oxide is pretty soluble, although it does not unite with the acid chemically. Only a small proportion, however, might be so removed. With a few samples of the gas freed from methyl acetate by means of strong sulphuric acid applied on a coke ball, the further action of fuming sulphuric acid was accordingly tried, and an absorption was obtained which I at first attributed to methyl oxide, or some such substance. On further examination, however, it was discovered that the diminution in volume was due to absorption of hydrogen by the sulphuric anhydride. The solution electrolysed contained 60 per cent. of potassium acetate, and in this experiment a hydrogen voltameter was introduced into the circuit for the sake of comparison. The electrolytic gas previous to the analysis was freed from carbonic anhydride by treating it in an absorber with caustic potash solution. The following are the details of the analysis:—

I.

	Observed volume.	Temp.	Bar., mm.	Reduced volume.
Original gas (CO_2 free)	4259·8	8·5° C.	738·0	3958·5
Treated with H_2SO_4	4197·3	8·3	746·5	3952·5
,, ,, SO_3 (12 hrs.)	4186·9	8·2	732·4	3916·5
,, ,, K pyrogallate	4206·6	8·4	724·8	3892·1

Hence: Methyl acetate (?) = 0·15 per cent.
,, oxide (?) = 0·91 ,,
Oxygen........ = 0·62 ,,

The residue was then analysed by exploding it with excess of oxygen and absorbing the carbonic anhydride produced, by means of caustic potash.

	Observed volume.	Temp.	Bar., mm.	Reduced volume.
Original gas	1589·4	7·8° C.	736·6	1496·6
With excess of oxygen	7519·5	8·1	737·6	7081·9
After combustion	4406·8	8·1	738·2	4157·0
After absorption of CO_2	2990·5	8·0	738·5	2823·1

These figures give the following results:—

x = carbonic anhydride formed on combustion.
y = total diminution in volume on combustion.

Then, ethane $= \frac{x}{2}$, and hydrogen $= \frac{2}{3}\left(y - \frac{x}{2} \cdot \frac{5}{2}\right)$.

$$\begin{array}{rl} \text{Ethane} = & 666{\cdot}9 \\ \text{Hydrogen} = & \underline{838{\cdot}5} \\ & 1505{\cdot}4 \end{array}$$

Corresponding voltameter hydrogen = 839·8.

From this we obtain the ratio $\frac{\text{ethane}}{\text{hydrogen}} = 0{\cdot}795$, and

$$\frac{\text{ethane}}{\text{volt. hydrogen}} = 0{\cdot}794.$$

II. *Same Solution Electrolysed.*

	Observed volume.	Temp.	Bar., mm.	Reduced volume.
Original gas (CO_2 free)	5310·8	7·8° C.	752·2	5109·8
Treated with H_2SO_4	5320·1	9·4	752·1	5088·6
,, ,, SO_3 (24 hrs.)	5272·3	8·3	743·2	4984·2
,, ,, K pyrogallate	5297·6	8·4	735·5	4973·8

Hence:

Methyl acetate (?) = 0·42 per cent.
,, oxide (?) = 2·04 ,,
Oxygen........ = 0·20 ,,

Analysis of Residue.

	Observed volume.	Temp.	Bar., mm.	Reduced volume.
Original gas	1526·3	8·4° C.	734·8	1431·6
With excess of oxygen	6431·4	8·4	734·6	6031·0
After combustion..............	3453·9	8·4	734·2	3236·5
After absorption of CO_2........	2083·9	8·4	733·5	1951·9

Hence:

Ethane = 642·3
Hydrogen = 792·5
1434·8

The corresponding voltameter hydrogen = 809·2.

$$\text{Ratio } \frac{\text{ethane}}{\text{hydrogen}} = 0{\cdot}813, \quad \frac{\text{ethane}}{\text{voltameter hydrogen}} = 0{\cdot}794.$$

Comparing the results in these two sets of analyses, we have—

	SO_3 in contact.	Methyl oxide (?).	$\frac{\text{Ethane}}{\text{hydrogen}}$.	$\frac{\text{Ethane}}{\text{voltameter hydrogen}}$.
I	12 hours	0·91	0·795	0·794
II	24 „	2·04	0·813	0·794

It was evident that the sulphuric anhydride was reacting with something else than methyl oxide in the gaseous mixture, for the longer the reagent remained in contact with the gas the greater was the absorption. The fact that the ratio ethane to hydrogen increased with the increased absorption, the ratio ethane to voltameter hydrogen remaining at the same time constant, pointed to the removal of hydrogen.

A quantity of pure hydrogen was therefore exposed for three days to the action of a coke ball soaked in strongly fuming sulphuric acid. A large absorption was obtained, as the following shows:—

	Observed volume.	Temp.	Bar., mm.	Reduced volume.
Original hydrogen	4739·2	6·6° C.	746·8	4547·0
After treatment with SO_3 (3 days).....................	4472·7	6·0	748·9	4312·6

Hydrogen absorbed = 234·4, or 5·1 per cent.

This fact is of great importance to gas analysts. Dittmar and Henderson found (*Proc. Phil. Soc. Glasgow*, Dec., 1890) that sulphuric acid was reduced by hydrogen to a very slight extent—too slight to affect experiments of this kind. The fuming acid is evidently much more powerful in its action; a quantity of hydrogen treated with ordinary strong sulphuric acid, under conditions similar to the above, showed an absorption of only 0·56 per cent.

The absorption which took place on treating the electrolytic gas with fuming sulphuric acid was thus evidently due—taking into consideration the time that the balls were in contact—to the absorption of hydrogen.

No methyl oxide that escapes absorption by ordinary strong sulphuric acid, and no unsaturated hydrocarbons, appear to be present in the electrolytic gas in measurable quantity; and this is borne out by the results obtained on the analysis of the gas treated with sulphuric acid alone, the analysis being carried out under the supposition that the mixture consisted of oxygen, ethane, and hydrogen. On warming the sulphuric acid balls withdrawn from the gas, the odour of acetic acid was very evident, as Kolbe found. There can be little doubt, therefore, that the ethereal salt present in the vapour is methyl acetate. Nothing further has been done regarding the detection of methyl formate or methyl carbonate.

Influence of the Concentration of Potassium Acetate on the Electrolysis.

A 60 per cent. solution of potassium acetate was prepared and acidified slightly with acetic acid. Less concentrated solutions were obtained from this by dilution with weighed quantities of water, so that the degree of acidity of the solutions was the same in all cases.

The electrolyses were conducted at temperatures lying between 11° and 12°. The gas to be analysed had the carbonic anhydride first removed, and was then exposed for about two hours to the action of a coke ball soaked in strong sulphuric acid. Oxygen was determined by absorption with alkaline pyrogallate of potash applied either on *papier-maché* balls, or the gas was shaken up in an absorber with a solution of pyrogallate. The residue, after removal of the ethereal vapour and oxygen, was analysed for ethane and hydrogen by combustion with oxygen. In shaking out the gas with caustic potash (to remove carbonic anhydride), it is probable that part of the methyl acetate is destroyed, so that the values determined for that substance from the absorption by sulphuric acid are of little quantitative importance. The fact that small quantities of other absorbable vapours may be present also renders the determination of this substance practically worthless.

TABLE I.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
P. c. KA in solution....................	60	49	27·47	19·07	11·77	6·7	3·58	1·84	0·97	0·50
P. c. methyl acetate	0·1	0·15	trace	trace	trace	—	—	—	—	—
P. c. oxygen	0·16	0·50	0·68	0·53	0·66	0·83	1·36	2·48	10·5	32·47
Ratio $\frac{\text{ethane}}{\text{hydrogen}}$, two determinations....	0·800 0·792	0·779 0·779	0·760 0·759	0·742 0·742	0·738 0·733	0·684 --	0·615 0·595	0·509 0·508	0·264 0·263	0·003 0·0026
Mean value............................	0·796	0·779	0·759	0·742	0·735	0·684	0·605	0·508	0·2635	0·0028

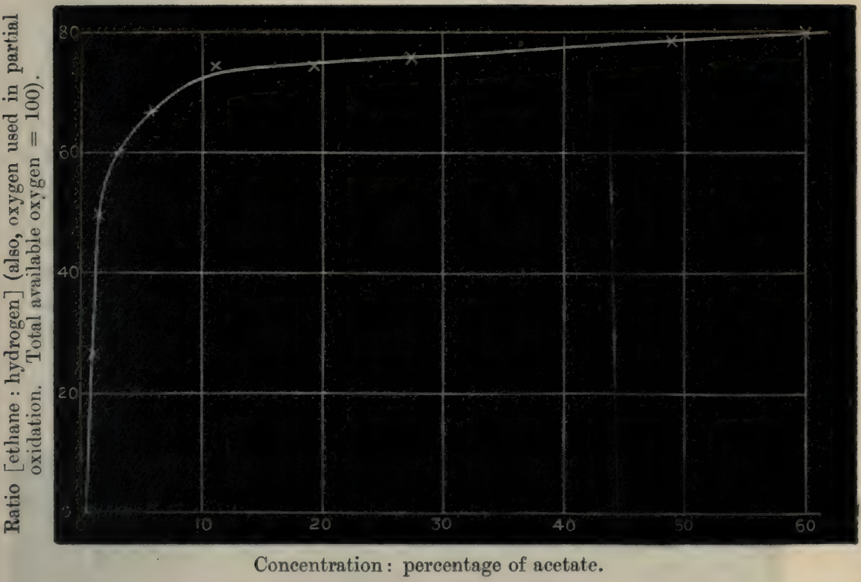
TABLE III.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Solution 1·5 per cent.	—	—	—	—	—	—	—	—	—	—
Current in ampères	2	2	2	2	2	1	0·4	0·4	0·4	0·4
Active surface of anode compared with that of cathode..............	1 : 1	1 : 12	12 : 1	1 : 110	110 : 1	1 : 1	1 : 12	12 : 1	1 : 12	12 : 1
Percentage of oxygen	0·3	trace	0·4	0·14	7·81	4·9	11·3	5·7	11·9	5·77
Ratio $\frac{\text{ethane}}{\text{hydrogen}}$	0·806	0·91	0·781	0·877	0·277	0·238 0·233 } 0·235	0·252 0·251 } 0·2515	0·238 0·231 } 0·2345	—	—

The nature of the electrolysis under the varying conditions is most conveniently indicated by the magnitude of the ratio ethane to hydrogen, and by the amount of oxygen present. Table I exhibits the results of the experiments on concentration of solution.

The relation between the amounts of ethane and hydrogen evolved, when different strengths of solution are electrolysed, may be seen from the curve represented in Fig. 1.

Fig. 1.—Curve exhibiting the relation between concentration of solution and the ratio [ethane : hydrogen] (also the relation between concentration and the proportion of the total oxygen = ½ hydrogen which has disappeared in partial oxidation, p. 34).



The percentage strengths of the solutions are taken as abscissæ, and the ratios ethane to hydrogen given in the table as ordinates.

From an inspection of the curve, it is seen that, starting with a saturated solution, and gradually diluting down to about a 10 per cent. solution, the fall in the quantity of ethane obtained is very small. Whilst the concentration has been reduced from 60 per cent. to 10 per cent., the quantity of ethane (hydrogen = 100) has only dropped from 80 to 72. With less than a 10 per cent. concentration, the amount of ethane produced falls off more rapidly, and below 2 per cent. the curve drops almost perpendicularly, cutting the horizontal axis about 0·5, so that with solutions of less than 0·5 per cent. no ethane is evolved, the gas being practically pure detonating gas.

Strength of Current.

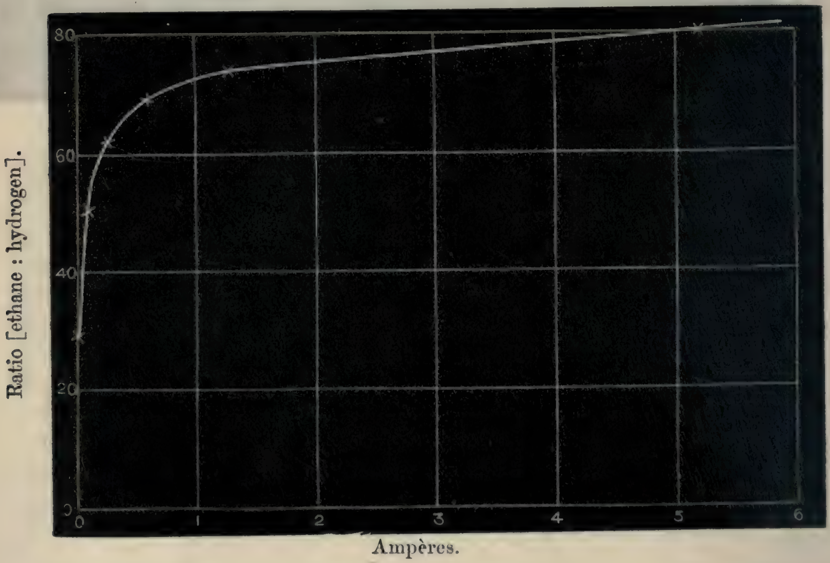
To determine what influence a change in the strength of the current has on the electrolysis, a 20 per cent. solution was electrolysed. The two electrodes were the same as before, but various strengths of current were employed. The results obtained are in entire agreement with theory. Methyl acetate was removed as in the preceding series of analyses, but its quantity was not determined. The results are tabulated in Table II.

TABLE II.

	I.	II.	III.	IV.	V.	VI.
Current in ampères.....	5·2	1·3	0·60	0·27	0·11	0·045
Percentage of oxygen...	0·47	0·53	0·42	0·44	0·71	1·15
Ratio $\frac{\text{ethane}}{\text{hydrogen}}$	0·81	0·74	0·69	0·63	0·51	0·256

Here again the relations are best exhibited by means of a curve. Taking as abscissæ the strength of the current in ampères, and as ordinates the ratios ethane to hydrogen, the curve represented in Fig. 2 is obtained.

FIG. 2.—Curve exhibiting the relation between strength of current and the ratios [ethane : hydrogen].



Its resemblance to the curve for concentration is at once evident. When the current is very large, the yield of ethane is little influenced by changes in the strength of the current, and just as dilute solutions are largely affected by alterations in the concentration, so slight variations in the strength of a weak current occasion considerable changes in the yield of ethane. The solutions are very sensitive to changes in the strength of the current when this sinks below 0·5 of an ampère.

The current, in these experiments, was reduced to the necessary strength by introducing resistances into the circuit, and it was found that the results were the same whether the resistances were introduced outside or inside the electrolytic cell. The electrolysis is, therefore, independent of difference of potential between the electrodes, as one would expect.

As regards oxygen, it will be noticed that its quantity remains pretty uniform throughout, only rising in the last two experiments. Although the ratio ethane to hydrogen is affected similarly by alterations in the strength of the current, and in the concentration of solution, the amount of oxygen, in the former case, does not rise with anything approaching the same rapidity as in the concentration experiments, so that the oxygens corresponding to given ratios of ethane to hydrogen in the two series are very different.

In the experiments on concentration, for a ratio of 0·509, the percentage of oxygen is 2·48, and for a ratio of 0·263 the percentage is 10·5. In the experiments on strength of current, on the other hand, the ratios 0·51 and 0·256 are associated with 0·71 per cent. and 1·15 per cent. of oxygen respectively.

This will be referred to again in considering the oxidation which goes on during the electrolysis.

Size of Electrodes.

It has already been mentioned that variations in the size of the electrodes will affect the concentration of the liberated ions, and, consequently, the nature of the electrolysis. As the reaction which gives rise to the ethane proceeds at the anode, it follows that variations in the size of the anode alone should influence the yield of ethane. Provided the size of the anode is kept constant, and also the current, then altering the size of the cathode should have no effect on the ratio ethane to hydrogen.

That the electrolysis proceeds in the manner indicated only when the anode is sufficiently small, is already known to be true for substances other than potassium acetate. Crum Brown and Walker have shown (*Trans. Roy. Soc. Edin.*, **35**, 214; *Annalen*, **261**, 111) that an aqueous solution of potassium ethyl malonate on electrolysis gives a good yield of ethyl succinate when the anode is very small, but only a trace if the anode is large.

This result, as they point out, contradicts the observation made by Jahn (*ibid.*, **37**, 422), that when sodium acetate is electrolysed, the yield of ethane is increased by increasing the size of the anode. I have succeeded in proving, beyond doubt, that the electrolysis of the acetate does not differ in this respect from that of potassium ethyl malonate, but that increasing the size of the anode diminishes the yield of ethane, as theory leads one to expect.

The solution of acetate employed here was a 20 per cent. neutral solution, and the current was of 2 ampères strength. Electrodes of various dimensions were used. The results are given in Table III (p. 20):—

In Experiments I and VI, the electrodes were those employed in the concentration experiments, each with an active surface of about 6 sq. cm. In II, III, VII, and VIII, one of these was replaced by a moderately thin platinum wire, with an active surface of about $\frac{1}{12}$ that of the other pole. In calculating the relative surfaces, it is assumed that the current flows from the whole surface of the wire, but only from one surface of the foil, namely, that which faces the other electrode. The active surfaces can, of course, be determined approximately only. In IV and V, the solution was electrolysed in a platinum crucible, which served as one of the electrodes, the other electrode being the platinum wire; the arrangement is the same as that employed by Crum Brown and Walker for the electrolysis of potassium ethyl malonate.*

In determining the influence on the electrolysis of a small or large anode, it is not sufficient to have two electrodes of different size, and then pass the current first in one direction and then in the reverse direction; for a much greater current is able to pass when the large electrode serves as the anode than when it is made the cathode. The probable reason of this is that at the anode a larger volume of gas is liberated than at the cathode, so that with the wire as anode the solution does not make such good contact as when the current is reversed, the wire then acting as cathode. For instance, in one case with a large anode and a small cathode, the current passing was 3·4 ampères; on reversing, it fell to 2 ampères. It is, therefore, necessary to adjust the external resistances so as to have equal currents flowing in each case.

In Experiments II and IV, the anodes were very small, and the ratios are the highest which I have obtained; in V, where there is a very large anode, the yield of ethane is small. By comparing I with III, and II with IV, it is evident that, so long as the anode is the same, changes in the size of the cathode have practically no influence on the electrolysis.

---

* The wire used was smaller than that employed by them as anode. They request me to state that the ratio of their electrodes was 30 : 1, not 300 : 1, as appears in their paper.

It has been remarked that one would expect the concentration of the acetions to be dependent on the current density at the anode, and on the strength of the solution. This is evidently not exclusively the case; for instance, according to the curve shown in Fig. 2 (p. 22), a current of 0·2 ampère gave, with an anode of active surface 12, a ratio of 0·61. In Experiment V of the above series, with a current of 2 ampères and an active surface 110, the ratio was 0·277. The current density at the anode in these two cases is practically the same. Whilst the ratios are as 0·61 : 0·277, the current densities are as 17 : 18.

Thus, although the yield of ethane is increased by increasing the current, or by employing a smaller anode, the variation is not to be accounted for by change in the current density alone. There are apparently some other factors influencing the electrolysis.

The amount of oxygen evolved increases with the fall in the ratio.

It was thought that by using a very dilute solution of the acetate, changing the size of the electrodes would, perhaps, have a greater effect than with a strong solution, seeing that a weak solution is very sensitive to changes in concentration. The influence of a large and small anode on a solution of 1·5 per cent. is seen in Experiments VI, VII, and VIII. Contrary to expectation, there is very little change in the ratio, but what change there is is in the expected direction. The yield of ethane is higher when the anode is small, but only a very little.

On the other hand, a remarkable change takes place in the quantity of oxygen evolved. Notwithstanding the slight difference in the ratios, the oxygen given off from the small anode is about double that given off from the large anode. The duplicate analyses IX and X confirm this.

Influence of Temperature.

Change of temperature cannot have any great influence on the electrolysis, as far as the concentration of the ions is concerned, but the nature of the secondary reactions must, like chemical reactions in general, be dependent on temperature. Table IV contains the results of the experiments on this point.

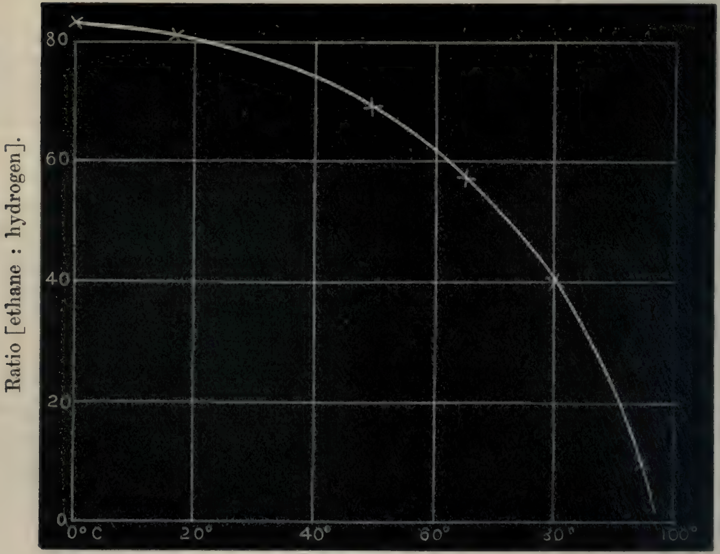
The solution employed contained 20 per cent. of the acetate, and the current in each case was 1·5 ampères.

The quantity of ethane produced gradually diminishes with rise of temperature, as may be seen from the curve Fig. 3 (p. 26), obtained by plotting the ratios ethane to hydrogen against temperature. The abscissæ represent temperature, and the ordinates the ratios of ethane to hydrogen. The diminution in ethane becomes more rapid as the temperature rises, and presumably about 100° the Kolbe reaction has entirely ceased.

TABLE IV.

	I.	II.	III.	IV.	V.	VI.
Temperature of experiment	0° C.	17°	50°	65°	80°	95°
Percentage of oxygen ...	0·27	0·31	0·40	0·61	4·17	25·64
Ratio $\frac{\text{ethane}}{\text{hydrogen}}$, two determinations	0·83 0·83	0·806 0·805	0·695 0·694	0·58 0·57	0·406 0·400	0·120 0·128
Mean value...........	0·83	0·8055	0·6945	0·575	0·403	0·124

FIG. 3.—Curve exhibiting the relation between temperature and the ratios [ethane : hydrogen].



Temperature.

As regards oxygen, the amount evolved increases with the fall in the ratio, but, on comparing the oxygen of the four series of experiments, it will be seen, as has already been pointed out in one instance, that the quantities of oxygen corresponding to a given ratio, as obtained by each of the four methods, are very different. For one particular ratio the oxygens are here compared:—

From experiments on	Ratio $\frac{\text{ethane}}{\text{hydrogen}}$.	Corresponding oxygen.
(*a.*) Concentration of solution	0·263	10·5 per cent.
(*b.*) Strength of current.....	0·256	1·15 „
(*c.*) Size of anode	0·277	7·81 „
(*d.*) Temperature	0·25	14·0 (approx. by interpolation).

Influence of Acid or Alkali.

The solution of acetate used in the experiments on concentration and strength of current was previously rendered slightly acid with acetic acid, chiefly that the results might be strictly comparable with those of other investigators. The solutions employed in the experiments on size of electrodes and on temperature were neutral.

It was found that the ratio ethane to hydrogen was slightly higher with the neutral than with the acid solution. The 20 per cent. acidified solution gave a ratio 0·74, whilst, for a neutral solution of the same strength, the ratio was 0·806. It was therefore thought advisable to examine into this point a little more closely. Two 2C per cent. solutions, one containing about 1·5 per cent. of free acetic acid, and the other an equal quantity of caustic potash, were electrolysed with the following results (Table V):—

TABLE V.

	I.	II.	III.	IV.
Solution	20 p. c. KA; 1·5 p. c. HA.	20 p. c. KA; 1·5 p.c. KOH.	20 p. c. KA; 1 p. c. K_2SO_4.	20 p. c. KA, neutral.
Percentage of oxygen .	1·3	0·51	0·17	0·3
Ratio $\frac{\text{ethane}}{\text{hydrogen}}$....	0·686 0·691	0·593 0·593	0·791 —	0·806 —
Mean value	0·688	0·593	0·791	0·806

The presence, therefore, of either acid or alkali, even in comparatively small quantity, considerably reduces the yield of ethane. That alkali produces this effect has already been proved by Bourgoin

(*Compt. rend.*, **65**, 998; *Jahresbericht*, 1867, 381), who showed that a solution containing 1 equivalent of potassium acetate to 1 of caustic potash, when electrolysed, yielded nothing but oxygen at the anode. It is noteworthy that the acid and alkali disturb the electrolysis in the same manner. More oxygen, however, is evolved from the acid than from the alkaline solution.

Experiment III in Table V (p. 27) shows that when small quantities of salts which give only hydrogen and oxygen on electrolysis, such as potassium sulphate, are present along with the acetate, the electrolysis is not appreciably affected. The presence of small quantities of chlorides gives rise to chlorinated organic compounds, such as methyl chloride (Kolbe).

It is a noticeable fact that the ratios of ethane to hydrogen obtained both by Kolbe and by Jahn are much smaller than the values found in this investigation. Kolbe used concentrated solutions of potassium acetate, and obtained the ratio 0·42 with 3 per cent. of oxygen, numbers agreeing with those for a very dilute solution, namely, 1·84 per cent., in the present concentration experiments. Jahn, with saturated solutions of the sodium salt, found values for the ratio lying in the neighbourhood of 0·5.

These investigators certainly employed weaker currents than I have done, but there is little doubt that the main cause of this great difference is the fact of their having used very large electrodes. Neither of them mentions the size of the anodes which were employed, but, from the description of Kolbe's apparatus, his anode must have been many times larger than mine.

Oxidation.

If the acetions by their interaction were to yield ethane and carbonic anhydride alone, then the volume of ethane obtained would be equal to the volume of hydrogen. Besides this reaction, however, and *Kolbe's second reaction*, there is, as already mentioned, the re-formation of acetic acid and liberation of oxygen (Faraday reaction), so that, under the most favourable conditions investigated, the volume of ethane is only nine-tenths that of the hydrogen. Neglecting the formation of methyl acetate, the excess of hydrogen over ethane represents the extent to which the Faraday electrolysis proceeds for any given strength of solution. If no further secondary reaction took place, then, for every volume of hydrogen that there is in excess of ethane, there ought to be half a volume of oxygen. But little or no oxygen is liberated except from dilute solutions. The oxygen is evidently used up in oxidising some portion of the electrolyte.

TABLE VI.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Percentage of KA in solution	60	49	27·47	19·07	11·77	6·7	3·58	1·84	0·97	0·50
Oxygen	0·16	0·50	0·68	0·53	0·66	0·83	1·36	2·48	10·50	32·47
Ethane	44·09	43·56	42·89	42·27	42·25	40·23	37·18	32·89	18·69	0·20
Hydrogen	55·75	55·94	56·43	57·20	57·09	58·94	61·46	64·63	70·81	67·33
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
A. Available oxygen....................	5·83	6·19	6·77	7·46	7·42	9·35	12·14	15·87	26·06	33·56
B. Oxygen which has disappeared	5·67	5·69	6·09	6·93	6·76	8·52	10 78	13·39	15·56	—
Ratio $\frac{B}{A}$	0·97	0·92	0·90	0·93	0·91	0·91	0·89	0·85	0·60	0·03

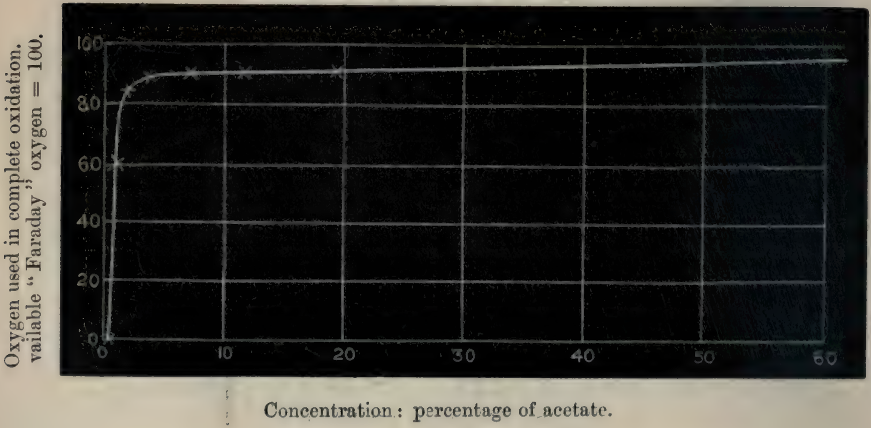
This was first pointed out by Kolbe (*Quart. J. Chem. Soc.*, **2**, 183; *Annalen*, **69**, 257), who showed that with the disappearance of oxygen there was a simultaneous increase in the quantity of carbonic anhydride evolved. From the data already given, it is possible to represent in a curve the relative amounts of oxygen which disappear on electrolysing solutions of different concentrations. Half the excess of hydrogen over ethane represents the total available electrolytic oxygen; the difference between this quantity and the oxygen actually found in the gas is the amount which has gone to oxidise the electrolyte.

By plotting the ratio [oxygen which has disappeared : available oxygen] against strength of solution, a curve is obtained which exhibits the relation between concentration of solution and oxidation by electrolytic oxygen. The ratio [oxygen which has disappeared : available oxygen] is calculated from the percentage composition of the gas evolved, obtainable from the foregoing analyses (Table I, p. 20). These percentage compositions and the ratios in question are given in the preceding table (Table VI) :—

The oxygen in II and III is a little high, probably owing to the fact that the values were determined by absorption with pyrogallate on *papier-maché* balls, whilst in the other cases the gas was treated in an absorber. In constructing the curve, II and III have therefore been neglected.

By taking the concentration as abscissæ, and the ratios given in the table as ordinates, the curve represented in Fig. 4 is obtained; it is very like that in Fig. 1, only the bend is much sharper, the change from oxidation to non-oxidation being very sudden.

FIG 4.—Curve exhibiting the relation between concentration and the proportion of "Faraday" oxygen which has disappeared.



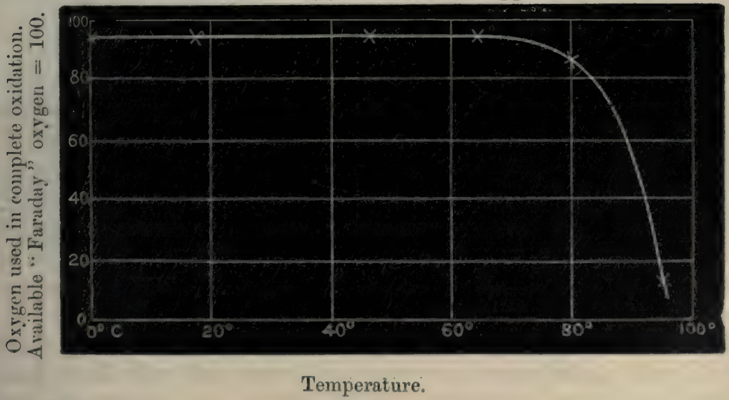
With a 0·5 per cent. solution, oxidation just begins, and it has almost reached its maximum with a 2—4 per cent. solution. The nearly constant value in the other curve is not reached until the solution has a strength of from 10 to 15 per cent.

Similarly, the curve obtained for oxidation when temperature is made to vary has been constructed, Fig. 5, from the following data (Table VII) :—

TABLE VII.

	I.	II.	III.	IV.	V.	VI.
Temperature centigrade.	0°	17°	50°	65°	80°	95°
Oxygen...............	0·27	0·31	0·40	0·89	4·17	25·64
Ethane	45·23	44·50	40·82	35·78	27·53	8·26
Hydrogen	54·50	55·19	58·78	63·33	68·30	66·10
	100·00	100·00	100·00	100·00	100·00	100·00
A. Available oxygen....	4·63	5·34	8·98	13·77	20·38	28·92
B. Oxygen which has disappeared	4·36	5·03	8·58	12·88	16·21	3·28
Ratio $\frac{B}{A}$	0·94	0·94	0·95	0·93	0·79	0·11

FIG. 5.—Curve exhibiting the relation between temperature and the proportion of "Faraday" oxygen which has disappeared.



The ratio here again represents the amount of oxygen used in oxidising the electrolyte, as compared with the total oxygen which would be evolved if no oxidation took place. These two curves show how the complete oxidation of the electrolyte to carbonic anhydride varies with the yield of ethane, so that the amount of oxidation diminishes with diminution in the yield of ethane. But it is evident that they change at different rates; in both instances the change in the amount of oxidation is more sudden than the change in the yield of ethane. It has also been pointed out that, in whatever way the conditions of the electrolysis may be altered, the yields of ethane and oxygen are differently affected. By comparing the oxidation curves themselves, it is seen that the oxidation falls off more rapidly with rise of temperature than with dilution of the solution. Oxidation curves, having for ordinates proportional oxidation, and for abscissæ strength of current and size of anode, respectively, have not been constructed; but from an examination of the values for oxygen, in the experiments on these points, it is evident that the most complete oxidation is obtained by varying the current. Whilst the ethane diminishes, according to the curve exhibited in Fig. 2 (p. 22), the oxidation continues uniform as far as the current was reduced, thus—

Current = 5·2 ampères. Ratio, = 0·81 Calculated oxidation = 91.
,, = 0·11 ,, ,, = 0·51 ,, = 96.
,, = 0·045 ,, ,, = 0·256 ,, = 96.
Perfect oxidation = 100.

When the anode varies, the oxidation is very much the same as when concentration varies. The different manner in which the oxidation is affected by changes in the individual conditions (namely, concentration, strength of current, size of anode, and temperature) is apparent at a glance, from the curves tabulated in Fig. 6. Here the proportional oxidations are plotted against the ratios ethane to hydrogen, obtained by varying in succession the four conditions in question.

It will be noticed that with a ratio of about 0·75, no matter by what means it is produced, the accompanying oxidation is always the same. For other ratios, however, the four conditions are seen to give rise to very different amounts of oxidation. The presence of alkali appears to favour oxidation.

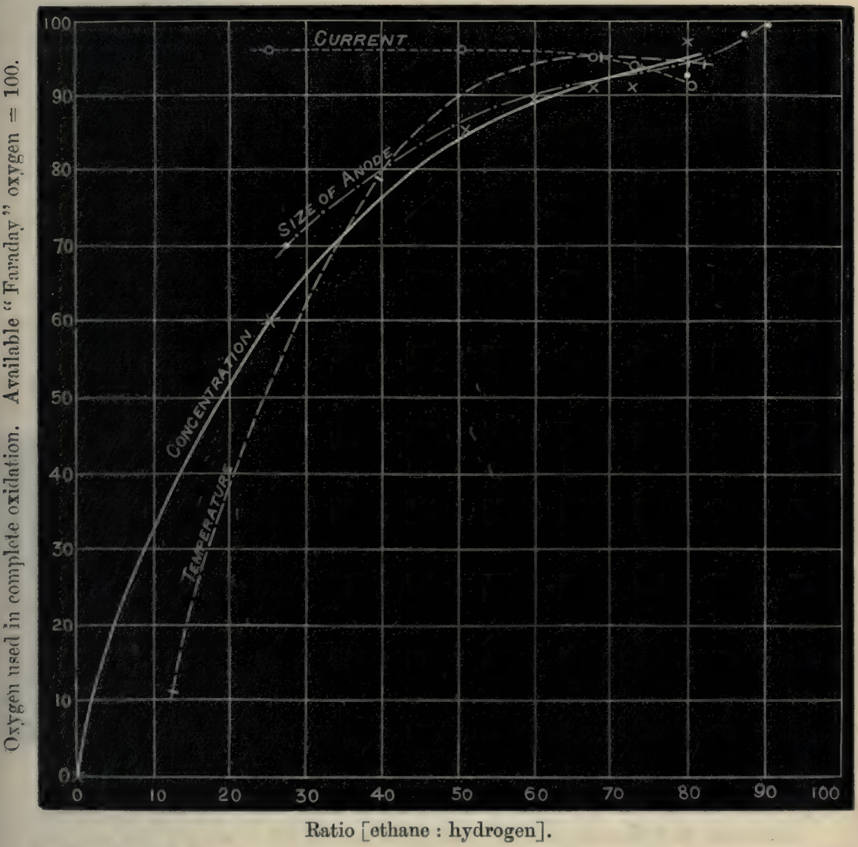
Besides the theory of the formation of ethane here adopted, there is, as already stated, another view, which originated with Kolbe himself, and which, in a somewhat modified form, is now supported by Bourgoin, Jahn, and Bunge. They consider the ethane to be produced by a partial oxidation of the acetic acid by the electrolytic oxygen.

It is assumed that acetic acid is first produced (according to the

Faraday electrolysis), and at the same time oxygen, and further that the oxygen attacks the acetic acid so formed, thus :—

$$2CH_3{\cdot}COOH + O = C_2H_6 + 2CO_2 + H_2O.$$

FIG. 6.—Curves exhibiting the relation between complete oxidation to carbonic acid, and the ratios [ethane : hydrogen] as produced by varying concentration, current, size of anode, and temperature.



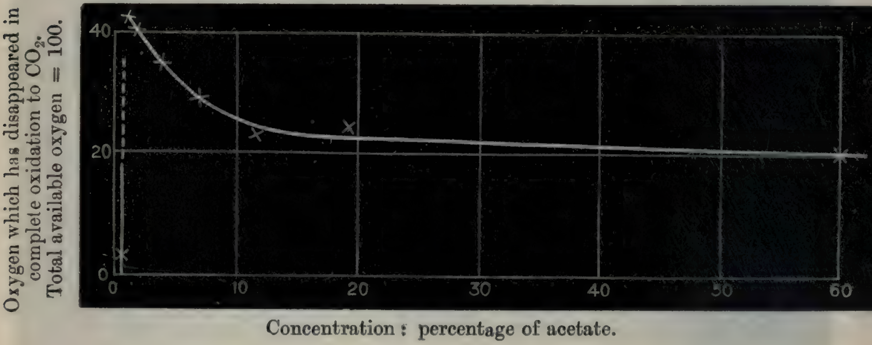
If the reaction were to proceed entirely according to this equation, then equal volumes of hydrogen and ethane would result from the electrolysis; but part of the acetic acid is completely oxidised to carbonic acid—

$$CH_3{\cdot}COOH + 4O = 2CO_2 + 2H_2O.$$

Such a conception of the nature of the reaction in question seems highly improbable. The method of explanation is, to say the least, somewhat roundabout; and, although it would be a difficult matter to disprove these assumptions, numerous facts point to the unlikelihood of their theory being the correct one. The oxidation theory does not afford a ready explanation of the formation of methyl acetate, or of the formation of butyl valerate in the electrolysis of potassium valerate. It would also appear that acetic acid is not easily oxidised by electrolytic oxygen, for a solution containing 10 per cent. of sulphuric acid and 10 per cent. of acetic acid when electrolysed was found to give scarcely a half per cent. of carbonic anhydride in the evolved gas.

Assuming the oxidation theory to be correct, it has already been shown that the amounts of the two reactions—the complete and the partial oxidations (ethane formation)—change at different rates with change of concentration, &c. Instead of plotting the proportional oxidation, that is, the amount of oxidation which takes place as compared with the total possible oxidation, we may tabulate the actual amount of oxygen used up for both oxidations as compared with the *total available* oxygen which is equal to half the hydrogen evolved. The curves are shown in Figs. 1 (p. 21) and 7. The oxygen for partial oxidation (ethane formation) is half the volume of ethane produced, and the oxygen for complete oxidation is simply the oxygen which has otherwise disappeared. Each of these series of values must be divided by the *total available* oxygen. The concentrations are plotted on the horizontal, and the oxidation ratios on the vertical, axis; available oxygen = 100. The partial oxidation curve is simply a reproduction of the concentration curve, Fig. 1. It is now evident that, on dilution, the amount of partial oxidation diminishes, while the amount of complete oxidation increases up to a certain point which is not determined, and then suddenly falls to zero. Jahn assumed in

FIG. 7.—Curve exhibiting the relation between concentration, and the proportion of th total oxygen (= ½ hydrogen) which has disappeared in complete oxidation to carbonic acid



support of the oxidation theory that the more condensed oxygen produced a more perfect oxidation; hence, by using a small anode, the oxidation would proceed further and the yield of ethane be reduced. His experimental results bearing on this point have already been contradicted, and as to the more highly condensed oxygen effecting a more perfect oxidation (so far as complete oxidation to carbonic anhydride, at least, is concerned) the oxidation curves, Figs. 1 and 7, point to the reverse being the case, namely, that with increased condensation the oxidation to carbonic anhydride is less complete.

An instance has also been given (p. 25) where a diminution in the size of the anode, that is, an increased current density, shows a diminished amount of complete oxidation, the partial oxidation (ethane formation) remaining constant.

In the experiments on strength of current, it was also conspicuously evident that large diminutions in the current produced very little change in the amount of oxygen evolved; the oxidation figures are themselves given on p. 32.

It would seem, therefore, that an increase in the current density lessens the amount of complete oxidation to carbonic anhydride, whilst, if the oxidation theory be true, it increases the amount of partial oxidation to ethane, which seems a very unlikely state of matters. For the complete oxidation of the acetic acid, eight times more oxygen is required than for the partial oxidation, and one would, therefore, expect the complete oxidation to cease first.

If the ethane is formed by the simple interaction of the acetions, and not by oxidation, the rise in the amount of complete oxidation (Fig. 7) is easily accounted for. As the ethane diminishes, the oxygen produced in the Faraday electrolysis increases in quantity; so that the increased oxidation is simply due to the presence of a larger supply of oxygen. As to the portion of the electrolyte which undergoes this complete oxidation, it cannot be acetic acid, for it has been seen that acetic acid is hardly attacked by electrolytic oxygen. The simplest view to take is that the acetions themselves suffer oxidation to carbonic anhydride.

Several experiments were made using equivalent solutions of potassium, sodium, and calcium acetates, and it was found that the ratios obtained by electrolysing these solutions were the same. The following are the figures:—

20·0 per cent. solution potassium acetate. Ratio $\frac{\text{ethane}}{\text{hydrogen}} = 0{\cdot}805.$
16·7 „ „ sodium „ „ „ $= 0{\cdot}810.$
15·1 „ „ calcium „ „ „ $= 0{\cdot}804.$

Acetates, therefore, whether they contain univalent or bivalent metals, are similarly affected by the electrolytic current. This is a proof that the formation of ethane is independent of the metal of the salt, but dependent only on the acetion.

I would take this opportunity of expressing my cordial thanks to Professor Crum Brown and Dr. James Walker for many important suggestions received during this investigation.

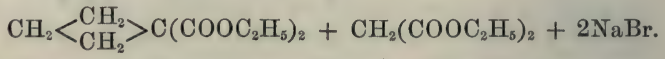
III.—CONTRIBUTIONS FROM THE LABORATORIES OF THE HERIOT WATT COLLEGE, EDINBURGH.

The Synthetical Formation of Closed Carbon Chains. Part II (continued). *Derivatives of Tetramethylene.*

By W. H. Perkin, Jun., Ph.D., F.R.S., and W. Sinclair, B.Sc.

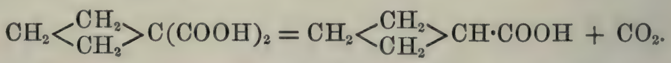
In a former research (Trans., 1887, **51**, 1), it was shown that trimethylene bromide reacts with the sodium compound of ethyl malonate with formation of ethyl tetramethylenedicarboxylate:

$$\mathrm{2CHNa(COOC_2H_5)_2 + CH_2Br{\cdot}CH_2{\cdot}CH_2Br =}$$



$$\mathrm{CH_2{<}\genfrac{}{}{0pt}{}{CH_2}{CH_2}{>}C(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 + 2NaBr.}$$

This ethereal salt, on hydrolysis, yields the corresponding bibasic acid, which, when heated above its melting point, is decomposed with elimination of carbonic anhydride and formation of tetramethylenemonocarboxylic acid:



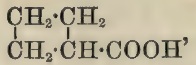
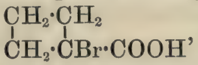
$$\mathrm{CH_2{<}\genfrac{}{}{0pt}{}{CH_2}{CH_2}{>}C(COOH)_2 = CH_2{<}\genfrac{}{}{0pt}{}{CH_2}{CH_2}{>}CH{\cdot}COOH + CO_2.}$$

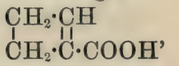
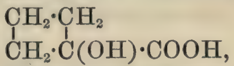
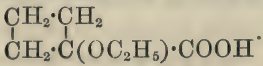
Owing to the formation of large quantities of ethyl pentanetetracarboxylate in the above reaction, the yield of tetramethylenecarboxylic acid obtained is so small that only those properties of the acid could be investigated which had a direct bearing on the question of its constitution.

During the course of some investigations on ethyl pentanetetracarboxylate, a considerable quantity of crude ethyl tetramethylenedicarboxylate accumulated, and we have taken this opportunity of studying the properties of tetramethylene derivatives more thoroughly.

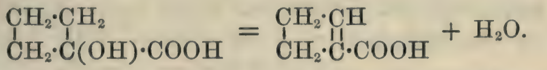
Tetramethylenecarboxylic acid is characterised by extreme stability, and all previous experiments instituted with a view to obtaining bromine and other substitution derivatives were unsuccessful.

Auwers and Bernhardi (*Ber.*, **24**, 2209) have lately studied the action of bromine on fatty acids in the presence of phosphorus (the so-called Hell-Volhard-Zelinsky method), and as the result of their experiments, these chemists are led to the conclusion that all acids which contain a hydrogen atom in the α-position readily form bromine substitution products, the bromine displacing the α-hydrogen atom.

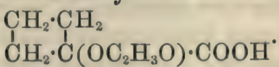
As tetramethylenecarboxylic acid,  $\begin{array}{l}CH_2\cdot CH_2\\ |\quad\;\; |\\ CH_2\cdot CH\cdot COOH\end{array}$, contains a hydrogen atom in the α-position, we have investigated the action of bromine on this acid in the presence of phosphorus, and we find that by this means an almost quantitative yield of monobromotetramethylenecarboxylic acid,  $\begin{array}{l}CH_2\cdot CH_2\\ |\quad\;\; |\\ CH_2\cdot CBr\cdot COOH\end{array}$, is obtained.

This acid has been very carefully investigated, as it appeared possible that under suitable conditions hydrogen bromide might be eliminated with formation of an unsaturated acid,  $\begin{array}{l}CH_2\cdot CH\\ |\quad\;\; \|\\ CH_2\cdot C\cdot COOH\end{array}$, the study of which would yield very interesting results. When digested with aqueous potassium hydrate solution, the bromo-acid yields hydroxytetramethylenecarboxylic acid,  $\begin{array}{l}CH_2\cdot CH_2\\ |\quad\;\; |\\ CH_2\cdot C(OH)\cdot COOH\end{array}$, very little, if any, of an unsaturated acid being produced; the action of alcoholic potash or of sodium ethylate converts the bromo-acid into ethoxytetramethylenecarboxylic acid,  $\begin{array}{l}CH_2\cdot CH_2\\ |\quad\;\; |\\ CH_2\cdot C(OC_2H_5)\cdot COOH\end{array}$.

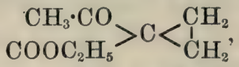
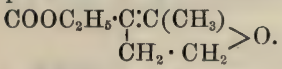
As these experiments did not lead to the desired result, our attention was turned to hydroxytetramethylenecarboxylic acid, because it was thought probable that dehydrating agents acting on this acid might remove the elements of water, forming the unsaturated acid, thus:—

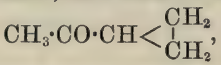
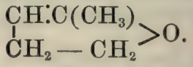


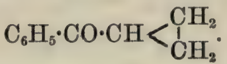
$$\begin{array}{l}CH_2\cdot CH_2\\ |\quad\;\; |\\ CH_2\cdot C(OH)\cdot COOH\end{array} = \begin{array}{l}CH_2\cdot CH\\ |\quad\;\; \|\\ CH_2\cdot C\cdot COOH\end{array} + H_2O.$$

Owing to the great stability of the hydroxy-acid, nothing but negative results have so far been obtained; sulphuric acid decomposes the acid with formation of *carbon monoxide.* Zinc chloride and other dehydrating agents convert the acid into high boiling products, and sodium acetate and acetic anhydride at 230° simply produce the corresponding acetate,  $\begin{array}{l}CH_2\cdot CH_2\\ |\quad\;\; |\\ CH_2\cdot C(OC_2H_3O)\cdot COOH\end{array}$.

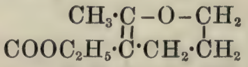
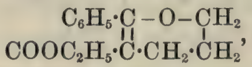
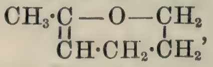
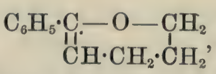
Further experiments on this subject are in progress.

The reaction between ethylene bromide and the sodium compound of ethyl acetoacetate has repeatedly been made the subject of investigation, and the examination of the primary product of the reaction appears to leave no doubt that this substance is ethyl acetyltrimethylenecarboxylate,  $\begin{array}{l}CH_3\cdot CO\\ COOC_2H_5\end{array}\!>\!C\!<\!\begin{array}{l}CH_2\\ |\\ CH_2\end{array}$, mixed with varying proportions of the isomeric ethyl methyldehydropentonecarboxylate,  $\begin{array}{l}COOC_2H_5\cdot C\colon C(CH_3)\\ \quad\;\; |\\ \quad\;\; CH_2\cdot CH_2\end{array}\!>\!O$.

Ethyl acetyltrimethylenecarboxylate, on hydrolysis, yields the corresponding acid; and this, on distillation, is converted into acetyltrimethylene,  $CH_3\cdot CO\cdot CH\!<\!\begin{array}{l}CH_2\\ |\\ CH_2\end{array}$, and carbonic anhydride; ethyl methyldehydropentonecarboxylate under similar conditions yields the isomeric methyldehydropentone,  $\begin{array}{l}CH\colon C(CH_3)\\ |\\ CH_2 - CH_2\end{array}\!>\!O$. Similarly, ethyl benzoyltrimethylenecarboxylate is produced by the action of ethylene bromide on the sodium compound of ethyl benzoylacetate; in this case, however, no trace of the isomeric ethyl phenyldehydropentonecarboxylic acid appears to be formed; the free benzoyltrimethylenecarboxylic acid, on distillation, is converted quantitatively into carbonic anhydride and benzoyltrimethylene,

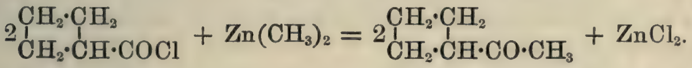


$$C_6H_5\cdot CO\cdot CH\!<\!\begin{array}{l}CH_2\\ |\\ CH_2\end{array}.$$

Trimethylene bromide also reacts readily with the sodium compounds of ethyl acetoacetate and ethyl benzoylacetate, in both instances with formation of dehydrohexone derivatives, that is, of ethyl methyldehydrohexonecarboxylate,  $\begin{array}{l}CH_3\cdot C - O - CH_2\\ \qquad \| \qquad\quad\; |\\ COOC_2H_5\cdot C\cdot CH_2\cdot CH_2\end{array}$ and ethyl phenyldehydrohexonecarboxylate,  $\begin{array}{l}C_6H_5\cdot C - O - CH_2\\ \qquad \| \qquad\quad\; |\\ COOC_2H_5\cdot C\cdot CH_2\cdot CH_2\end{array}$, no trace of the isomeric tetramethylene derivatives being produced, and the acids obtained by the hydrolysis of these ethereal salts yield, on distillation, methyldehydrohexone,  $\begin{array}{l}CH_3\cdot C - O - CH_2\\ \qquad \| \qquad\quad\; |\\ \qquad CH\cdot CH_2\cdot CH_2\end{array}$, and phenyldehydrohexone,  $\begin{array}{l}C_6H_5\cdot C - O - CH_2\\ \qquad \| \qquad\quad\; |\\ \qquad CH\cdot CH_2\cdot CH_2\end{array}$, respectively.

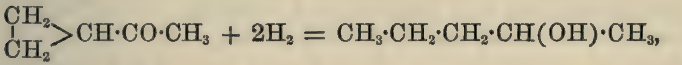
As it is therefore not possible to obtain keto-derivatives of tetramethylene corresponding to acetyltrimethylene (trimethylene methyl ketone) and benzoyltrimethylene (trimethylene phenyl ketone) by this means, it appeared to us that it would be interesting to endeavour to prepare these substances from tetramethylenecarboxylic acid, in order to be able to institute a direct comparison between the two series of ketones. The following are the results of our experiments :—

Tetramethylenecarboxylic chloride reacts very readily with zinc methide with formation of tetramethylene methyl ketone :



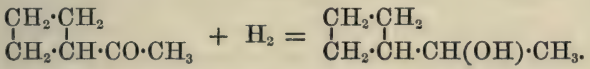
$$2\begin{array}{l}CH_2\cdot CH_2\\ |\qquad\ |\\ CH_2\cdot CH\cdot COCl\end{array} + Zn(CH_3)_2 = 2\begin{array}{l}CH_2\cdot CH_2\\ |\qquad\ |\\ CH_2\cdot CH\cdot CO\cdot CH_3\end{array} + ZnCl_2.$$

This interesting compound boils at 134°, or about 22° higher than trimethylene methyl ketone (b. p. 112°), and there is a considerable similarity between the two substances, those properties of the latter which are dependent on the instability of the trimethylene ring being naturally absent in the stable tetramethylene compound. In their behaviour towards reducing agents, for example, the two ketones differ widely. Trimethylene methyl ketone, when reduced by sodium in moist ethereal solution, is converted into propylmethylcarbinol (Trans., 1891, **59**, 874) :



$$\begin{array}{l}CH_2\\ |\\ CH_2\end{array}\!\!>CH\cdot CO\cdot CH_3 + 2H_2 = CH_3\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CH_3,$$

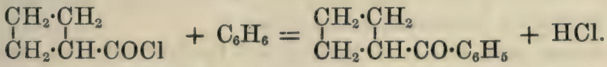
whereas tetramethylene methyl ketone, under precisely similar circumstances, yields the corresponding tetramethylenemethylcarbinol :



$$\begin{array}{l}CH_2\cdot CH_2\\ |\qquad\ |\\ CH_2\cdot CH\cdot CO\cdot CH_3\end{array} + H_2 = \begin{array}{l}CH_2\cdot CH_2\\ |\qquad\ |\\ CH_2\cdot CH\cdot CH(OH)\cdot CH_3.\end{array}$$

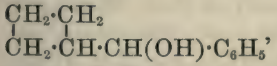
And, again, other reagents such as fuming hydrobromic acid and boiling dilute hydrochloric acid, which so readily decompose the trimethylene ring, appear to have no action whatever on tetramethylene methyl ketone.

This interesting point is again clearly brought out on comparing the properties of trimethylene phenyl ketone with those of tetramethylene phenyl ketone. The latter may be readily prepared by treating a solution of tetramethylenecarboxylic chloride in benzene with aluminium chloride, thus :—



$$\begin{array}{l}CH_2\cdot CH_2\\ |\qquad\ |\\ CH_2\cdot CH\cdot COCl\end{array} + C_6H_6 = \begin{array}{l}CH_2\cdot CH_2\\ |\qquad\ |\\ CH_2\cdot CH\cdot CO\cdot C_6H_5\end{array} + HCl.$$

It is a colourless oil boiling at 258—259°, or about 18° higher than the corresponding trimethylene phenyl ketone (b. p. 239—240°, 720 mm.). On reduction, it yields tetramethylenephenylcarbinol, $\begin{array}{l}CH_2\cdot CH_2\\ |\qquad\ |\\ CH_2\cdot CH\cdot CH(OH)\cdot C_6H_5\end{array}$, whereas trimethylene phenyl ketone under similar conditions is converted into propylphenylcarbinol,

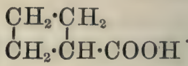


$C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$ (Trans., 1891, **59**, 885). In their behaviour towards fuming hydrobromic acid, again, these ketones differ widely, as, under these circumstances, trimethylene phenyl ketone yields benzoylpropyl bromide, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$, whereas tetramethylene phenyl ketone is not acted on by this reagent.

Several other interesting compounds are described in this paper, and a special point has been made of the study of the magnetic rotation of the substances obtained.

The magnetic rotation and also the density determinations, which were made most carefully by W. H. Perkin, sen., have again proved most valuable as a means of discriminating between closed chain derivatives and unsaturated compounds, and they show in the clearest manner how very similar these tetramethylene compounds are to ordinary saturated compounds of the fatty series containing 2 atoms of hydrogen more.

Tetramethylenemonocarboxylic Acid,



$$\begin{array}{l}CH_2{\cdot}CH_2\\ |\qquad\ \ |\\ CH_2{\cdot}CH{\cdot}COOH\end{array}$$

The preparation and properties of this acid have been briefly described in a former communication (Trans., 1887, **51**, 1). In preparing large quantities of it, the following method has been found to give good results.

320 grams of ethyl malonate is dissolved in a cold solution of 46 grams of sodium in 550 grams of absolute alcohol, 210 grams of trimethylene bromide added, and the whole allowed to stand, in a capacious flask connected with a reflux apparatus, until the somewhat violent reaction which soon sets in has subsided. The product, which should be quite neutral, is heated on a water-bath until the bulk of the alcohol has distilled over, when the residue is mixed with water and extracted three times with ether; the ether is then evaporated, and the resulting thick oil, which consists of a mixture of ethyl tetramethylenedicarboxylate, ethyl pentanetetracarboxylate, and unchanged ethyl malonate, is subjected to rapid distillation in a current of steam until no more oily drops pass over with the condensed water. The distillate is extracted three times with ether, the ethereal solution dried over calcium chloride, evaporated, and the colourless, oily residue purified by fractional distillation.

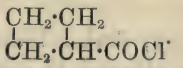
The fraction 180—240° is hydrolysed by boiling with twice the calculated quantity of alcoholic potassium hydrate for two hours, the alcohol distilled off, the residue mixed with water, evaporated on a water-bath till quite free from alcohol, acidified, and extracted five times with pure ether. The ethereal solution is then dried over calcium chloride, evaporated, and the residual crude tetramethylene dicarboxylic acid distilled in quantities of about 50 grams at a time and thus decomposed into carbonic anhydride and tetramethylenemonocarboxylic acid. The crude monobasic acid thus obtained is then further purified by fractional distillation, the portion boiling between 192° and 197° being used in subsequent experiments. The yield of tetramethylenemonocarboxylic acid obtained by this method is about 130 grams from 1 kilo. of ethyl malonate or about 40 per cent. of the theoretical yield. Freund and Gudeman (*Ber.*, **21**, 2694), using a slightly different method, state that they obtained only 8 per cent. of the theoretical yield.

In connection with this research, Dr. Walker has kindly determined the dissociation constants for the electrical conductivity of tetramethylenedicarboxylic acid and tetramethylenemonocarboxylic acid, with the following results:—

Tetramethylenedicarboxylic acid [1 : 1] ...... K = 0·0834.
Tetramethylenemonocarboxylic acid .... K = 0·00182.

It is interesting to note, as demonstrating the saturated nature of these substances, that solutions of the pure acids in sodium carbonate do not decolorise potassium permanganate even on long standing.

Tetramethylenecarboxylic Chloride,



$$\begin{array}{l} CH_2\cdot CH_2 \\ |\qquad\ \ | \\ CH_2\cdot CH\cdot COCl \end{array}.$$

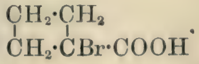
This substance, which has been obtained in small quantities by Freund and Gudeman (*Ber.*, **21**, 2696), is best prepared as follows:—

20 grams of the pure acid and 11 grams of freshly distilled phosphorus trichloride are heated by means of an oil-bath in a flask connected with a reflux condenser for half an hour, the temperature being so regulated that the mixture just boils. The product is carefully decanted from the layer of phosphorous oxide which forms, and twice fractioned. In this way, 20 grams of pure tetramethylenecarboxylic chloride are obtained boiling constantly at 137—139° (Freund and Gudeman give the boiling point as 142—143°); this, on analysis, gave the following result:—

0·2021 gram substance, heated with nitric acid and silver nitrate in a sealed tube at 150—160° for two hours, gave 0·2455 gram AgCl.

	Theory. C_5H_7OCl.	Found.
Cl	29·95 per cent.	30·07 per cent.

Monobromotetramethylenecarboxylic Acid,



$$\begin{array}{l} CH_2\cdot CH_2 \\ |\qquad\ \ | \\ CH_2\cdot CBr\cdot COOH \end{array}.$$

As stated in the introduction, this acid is readily prepared by acting on tetramethylenecarboxylic acid with bromine in the presence of phosphorus. The apparatus employed in our experiments on the bromination of tetramethylenecarboxylic acid consisted of a round-bottomed flask of about 300 c.c. capacity, connected with a Liebig's condenser by means of a piece of stout rubber tubing stretched over the end of the condensing tube, and inserted into the neck of the flask so as to make a tight joint, and at the same time expose only a very small surface of india-rubber to the action of the bromine and hydrogen bromide vapours. A dropping funnel, fitted with a long delivery tube, was inserted loosely in the open end of the upright condenser.

50 grams of pure tetramethylenecarboxylic acid was mixed with 3 grams of dry amorphous phosphorus in the flask, and 150 grams of bromine added very slowly from the dropping funnel; the reaction took place at once with considerable evolution of heat, and much hydrogen bromide escaped from the end of the condenser. As soon as the whole of the bromine had been added (the operation takes about two hours), the flask was gently heated by means of a paraffin-bath for about three hours, the condenser was then removed, and the heating continued until all traces of bromine vapour had disappeared.

The heavy, dark-coloured, oily product was well cooled, poured into water, allowed to stand for 10 minutes, extracted three times with ether, the ethereal solution filtered from a few black specks which are usually present, washed with water, and carefully dried over calcium chloride. After distilling off the ether, a yellowish oil remained, which, on distillation under reduced pressure, passed over almost entirely between 150° and 155° under a pressure of 70 mm., as a colourless oil which, on standing, solidified to a mass of crystals. These were spread on a porous plate until the traces of oily mother liquor present had been entirely absorbed, dried over sulphuric acid under reduced pressure, and analysed with the following results:—

I. 0·2004 gram substance gave 0·0750 gram H_2O and 0·3467 gram CO_2.

0·4220 gram substance, heated with nitric acid and silver nitrate at 200° for three hours, gave 0·4392 gram AgBr.

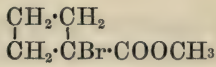
II. 0·2810 gram substance gave 0·2930 gram AgBr.

	Theory. $C_5H_7BrO_2$.	Found. I.	Found. II.	
C	33·52 per cent.	33·57	—	per cent.
H	3·91 ,,	4·15	—	,,
Br	44·70 ,,	44·25	44·40	,,

Monobromotetramethylenecarboxylic acid melts at about 48—50°, and the liquid, on cooling, solidifies to a mass of beautiful, colourless, pearly plates which have a faint butyric odour. It is readily soluble in alcohol, ether, and warm light petroleum, but only sparingly in water, although it is readily decomposed by boiling with this solvent with formation of hydrobromic acid. It dissolves readily in dilute aqueous potassium hydrate solution, and, on acidifying the solution, is deposited again as an oil. On boiling the alkaline solution, however, it is rapidly decomposed with formation of hydroxytetramethylenecarboxylic acid (p. 44). A crystal of the acid, placed on the surface of a dilute solution of sodium carbonate, rotates vigorously, and gradually dissolves; the solution of the sodium salt thus produced does not decolorise potassium permanganate, even on long standing.

The yield of the monobromo-acid obtained by the above method is very good; in two cases over 77 grams of the almost pure acid, boiling at 150—155° (70 mm.), was obtained from 50 grams of the tetramethylenecarboxylic acid, whereas theoretically it should have been 90 grams

Methyl Monobromotetramethylenecarboxylate,



$$\begin{array}{l} CH_2\cdot CH_2 \\ | \qquad\;\; | \\ CH_2\cdot CBr\cdot COOCH_3 \end{array},$$

In the first experiments on the bromination of tetramethylenecarboxylic acid, the crude product of the action of bromine on 27 grams of the pure acid (see previous section) was poured into an excess of methyl alcohol instead of into water. The reason for this was that, as the methyl salt must boil at a very much lower temperature than the acid itself, it was thought that the salt would be less liable to decompose on distillation. After standing for about one hour, the methyl alcohol solution was poured into a large quantity of water, extracted with ether, the ethereal solution washed with water containing a little sodium carbonate, and then dried over calcium chloride. The ethereal solution, after being filtered from a small quantity of a black, flocculent impurity, was evaporated, and the residual, slightly-brownish oil, which weighed 51 grams, distilled under reduced pressure. Almost the whole passed over between 115° and 120°, under a pressure of 100 mm., and on repeated fractionation, the methyl salt was obtained pure as a colourless oil boiling constantly at 117—119° (100 mm.). The analysis gave the following numbers :—

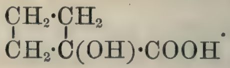
0·1388 gram substance gave 0·0630 gram H_2O and 0·1867 gram CO_2.

0·2385 gram substance, treated with nitric acid and silver nitrate at 180—190° for three hours, gave 0·2739 gram AgBr.

	Theory. $C_6H_9BrO_2$.	Found.
C	37·31 per cent.	36·92 per cent.
H	4·67 ,,	5·04 ,,
Br	41·45 ,,	41·00 ,,

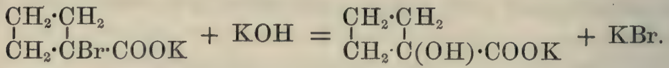
Methyl monobromotetramethylenecarboxylate is a heavy, colourless oil, which, when pure, may be distilled in small quantities under the ordinary pressure with only slight decomposition. The yield obtained by the above method is about 90 per cent. of the theoretical.

Hydroxytetramethylenecarboxylic Acid,



$$\begin{array}{l} CH_2\cdot CH_2 \\ |\qquad\ \ | \\ CH_2\cdot C(OH)\cdot COOH \end{array}.$$

This interesting acid is produced when monobromotetramethylenecarboxylic acid is boiled with aqueous potassium hydrate solution:



$$\begin{array}{l} CH_2\cdot CH_2 \\ |\qquad\ \ | \\ CH_2\cdot CBr\cdot COOK \end{array} + KOH = \begin{array}{l} CH_2\cdot CH_2 \\ |\qquad\ \ | \\ CH_2\cdot C(OH)\cdot COOK \end{array} + KBr.$$

35 grams of the pure bromo-acid was dissolved in cold, moderately-dilute potassium hydrate solution, and heated to boiling in a flask connected with a reflux apparatus, small quantities of strong potassium hydrate being added from time to time in order to keep the liquid always distinctly alkaline. At the end of about two hours, the solution was evaporated to a fairly small bulk, acidified with dilute hydrochloric acid, and extracted at least 20 times with pure ether; the ethereal solution was then dried over calcium chloride, evaporated, and the residual thick, oily acid purified by distillation under reduced pressure (50 mm.). The thermometer rose rapidly to 140°, between which temperature and 155° a small quantity of a colourless oil passed over; but the greater portion distilled between 205° and 210°; the thermometer then rose rapidly to 260°, the last fraction becoming completely solid on standing. The fraction 205—210° gave, on analysis, the following numbers:—

0·2333 gram substance gave 0·1482 gram H_2O and 0·4414 gram CO_2.

	Theory. $C_5H_8O_3$.	Found.
C	51·72 per cent.	51·60 per cent.
H	6·90 ,,	7·06 ,,
O	41·38 ,,	41·34 ,,

Hydroxytetramethylenecarboxylic acid is a thick, colourless syrup, so thick that a test-tube containing a few grams of it may be inverted without the syrup falling out. It is miscible with water in all proportions, and very difficult to completely extract from its aqueous solution by treatment with ether. The acid reduces ammoniacal silver solution very readily on warming, but not Fehling's solution even on boiling.

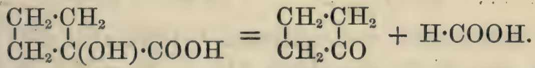
The basicity of the acid was determined by titration with standard potassium hydrate solution.

0·9946 gram of the pure acid required for neutralisation 86 c.c. of potassium hydrate solution (1 c.c. = 0·00559 gram KOH = 0·4807 gram KOH).

A monobasic acid of the formula $C_5H_8O_3$ requires 0·4804 gram KOH.

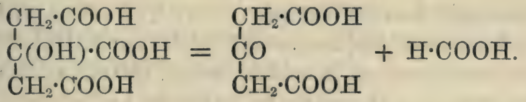
The salts of hydroxytetramethylenecarboxylic acid are almost all very readily soluble in water. Silver nitrate, copper, zinc, and lead acetates, barium and calcium chlorides give no precipitate with a moderately dilute neutral solution of the potassium salt. Hydroxytetramethylenecarboxylic acid dissolves in concentrated sulphuric acid with evolution of heat, and on standing a brisk effervescence takes place, due to the escape of *carbon monoxide.*

It is extremely probable that this remarkable phenomenon is due to the decomposition of the hydroxy-acid into formic acid (CO + H_2O) and ketotetramethylene, thus :—



$$\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot C(OH)\cdot COOH\end{array} = \begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CO\end{array} + H\cdot COOH.$$

A reaction of this nature would be exactly analogous to the formation of acetonedicarboxylic acid from citric acid (Pechmann, *Ber.*, **18**, 2289) and similar to that of cumalinic acid from malic acid (Pechmann, *Ber.*, **17**, 936) ; the first of these reactions takes place as follows :—

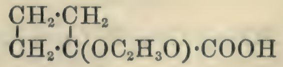


$$\begin{array}{l}CH_2\cdot COOH\\ C(OH)\cdot COOH\\ CH_2\cdot COOH\end{array} = \begin{array}{l}CH_2\cdot COOH\\ CO\\ CH_2\cdot COOH\end{array} + H\cdot COOH.$$

Owing to the small quantity of material at our disposal, this interesting decomposition has as yet not been further studied.

The yield of the distilled hydroxytetramethylenecarboxylic acid obtained in the above experiment was not good, at most about 35 per cent. of the theoretical yield. The lower boiling fractions and the solid substance mentioned above have not been further examined.

Acetoxytetramethylenecarboxylic Acid,



$$\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot C(OC_2H_3O)\cdot COOH\end{array}$$

In the course of experiments instituted with the object of eliminating the elements of water from hydroxytetramethylenecarboxylic acid, a quantity of this acid was heated with sodium acetate and a large excess of acetic anhydride in a sealed tube at 200—230° for four hours.

The product was distilled until the greater bulk of the acetic anhydride had been removed, the residue cooled well, mixed with water, allowed to stand for some time, and extracted four times with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a brownish oil; on fractionating this under reduced pressure, an almost colourless oil passed over, boiling at 200—220° (40 mm.), which on standing solidified almost entirely. The crystalline cake was spread on a porous plate to remove oily mother liquor, recrystallised from light petroleum, dried over sulphuric acid under reduced pressure, and analysed with the following result:—

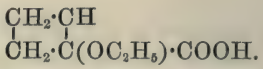
I. 0·1495 gram substance gave 0·0880 gram H_2O and 0·2914 gram CO_2.

II. 0·1769 gram substance gave 0·1036 gram H_2O and 0·3447 gram CO_2.

	Theory. $C_7H_{10}O_4$.	Found. I.	Found. II.
C	53·17 per cent.	53·16	53·14 per cent.
H	6·33 ,,	6·54	6·50 ,,
O.......	40·50 ,,	40·30	40·36 ,,

This substance is acetoxytetramethylenecarboxylic acid. It crystallises from light petroleum (b. p. 68—70°) in groups of slender needles which melt at 72—74°. It is excessively soluble in benzene, alcohol, and ether, readily so in boiling light petroleum, but only sparingly in the latter in the cold. It dissolves readily in cold water, and is evidently very easily hydrolysed. The composition of this acid was further proved by hydrolysis with standard potassium hydrate solution (1 c.c. = 0·00559 gram KOH). 0·8316 gram of the acetate was dissolved in a little water, 150 c.c. of the potassium hydrate solution added, the mixture boiled for an hour in a reflux apparatus, and neutralised with standard sulphuric acid. It was thus found that 106·7 c.c. of the potassium hydrate solution had been neutralised during the hydrolysis; this corresponds to 0·5964 gram KOH, whereas the amount required to neutralise the hydroxytetramethylenecarboxylic acid and the acetic acid produced from the acetate would theoretically be 0·5893 gram KOH.

Ethoxytetramethylenecarboxylic Acid,



$$\begin{array}{l} CH_2\cdot CH \\ | \quad\;\; | \\ CH_2\cdot C(OC_2H_5)\cdot COOH. \end{array}$$

If in the hydrolysis of monobromotetramethylenecarboxylic acid alcoholic instead of aqueous potash is employed, a substance is obtained which boils constantly at 230—232° under the ordinary pressure; this, on analyis, gave numbers agreeing approximately with those required for ethoxytetramethylenecarboxylic acid, and it appeared to us interesting to determine whether by employing sodium ethylate instead of alcoholic potash, this ethoxy-acid might not be obtained in a pure state. 60 grams of methyl monobromotetramethylenecarboxylate was added to a solution of 16 grams of sodium in 200 grams of absolute alcohol, and the product boiled for two hours in a flask connected with a reflux apparatus. The solution, which contained a quantity of sodium bromide in suspension, was evaporated until the excess of alcohol had been removed, the residue dissolved in water, acidified with hydrochloric acid, and extracted 10 times with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a slightly brownish oil which, on fractioning under reduced pressure (60 mm.), distilled for the most part between 160° and 175°. The colourless oil obtained on redistillation boiled at 164—165° (60 mm.), and, on analysis, gave the following numbers :—

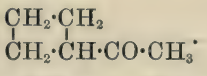
I. 0·1996 gram substance gave 0·1500 gram H_2O and 0·4237 gram CO_2.

II. 0·1520 gram substance gave 0·1155 gram H_2O and 0·3240 gram CO_2.

	Theory. $C_7H_{12}O_3$.	Found. I.	Found. II.
C	58·33 per cent.	57·89	58·13 per cent.
H	8·33 ,,	8·35	8·44 ,,
O	33·33 ,,	33·76	33·43 ,,

Ethoxytetramethylenecarboxylic acid is a thick, colourless liquid which is readily soluble in water; it seems to be decomposed by boiling with aqueous potassium hydrate solution with formation of hydroxytetramethylenecarboxylic acid.

Tetramethylene Methyl Ketone,



$$\begin{array}{l} CH_2{\cdot}CH_2 \\ | \quad\;\;\; | \\ CH_2{\cdot}CH{\cdot}CO{\cdot}CH_3 \end{array}.$$

This substance was readily prepared as follows :—15 grams of zinc methide was mixed with 50 grams of very carefully dried ether, 18 grams of pure tetramethylenecarboxylic chloride very slowly added, the temperature being kept below 30° by external cooling, and every precaution taken to exclude air and moisture as much as possible. At the end of about half an hour, water was cautiously added, the mixture allowed to stand for some time, the ethereal solution evaporated, and the residual almost colourless oil purified by distillation in a current of steam. The distillate was saturated with potassium carbonate, extracted several times with ether, the ethereal solution evaporated, and the crude ketone purified in the following way:—

In order to remove traces of methyl tetramethylenecarboxylate, (produced by the action of $Zn(OCH_3)_2$ on the tetramethylenecarboxylic chloride, see p. 52), the oil was digested in alcoholic solution for 20 minutes with a small quantity of pure potassium hydrate, the ketone precipitated by the addition of water, extracted with ether, the ethereal solution well washed with water, dried over calcium chloride, evaporated, and the residual oil submitted to fractional distillation. In this way, about 11·6 grams of colourless oil was obtained boiling constantly at 134° (738 mm.).

The analysis gave the following results:—

I. 0·1024 gram substance gave 0·0977 gram H_2O and 0·2744 gram CO_2.

II. 0·1365 gram substance gave 0·1282 gram H_2O and 0·3670 gram CO_2.

	Theory. $C_6H_{10}O$.	Found. I.	Found. II.
C	73·47 per cent.	73·08	73·32 per cent.
H	10·20 ,,	10·60	10·43 ,,
O	16·33 ,,	16·32	16·25 ,,

Tetramethylene methyl ketone is a colourless mobile oil, sparingly soluble in water, and possessing a strong odour of peppermint; it combines with sodium hydrogen sulphite very readily, forming a beautifully crystalline, pearly double compound, which resembles acetone sodium hydrogen sulphite in appearance.

The density and magnetic rotation determinations gave the following results:—

Density.—$d\,4°/4° = 0·9160$; $d\,5°/5° = 0·9155$; $d\,10°/10° = 0·9106$; $d\,15°/15° = 0·9065$; $d\,20°/20° = 0·9028$; $d\,25°/25° = 0·8994$.

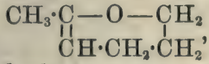
Magnetic Rotations.

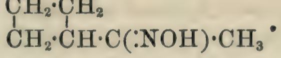
	t.	Sp. rotation.	Mol. rotation.
	15·5°	0·9837	5·911
	15·5	0·9823	5·902
	15·5	0·9808	5·893
	16·5	0·9852	5·924
	16·5	0·9837	5·915
	19·7	0 9754	5·880
	19·7	0 9792	5·903
	19·7	0·9784	5·898
	19·7	0·9754	5·880
Average ..	17·6	0·9805	5·901

Comparing the magnetic rotation of tetramethylene methyl ketone with that of the nearest saturated ketone, that is, methyl butyl ketone, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$, we find that the former possesses a rotation even smaller than the latter; thus:—

Methyl butyl ketone (calc.)	6·522
Less H_2 for difference in composition	0·508
	6·014
Tetramethylene methyl ketone	5·901
Difference	0·113

This shows at once that tetramethylene methyl ketone cannot be an unsaturated substance, because unsaturated substances invariably have much higher rotations than the corresponding saturated substances (compare W. H. Perkin, sen., Trans., 1889, **55**, 733—734). In a previous research on the products formed by the distillation of calcium tetramethylenecarboxylate with lime (Colman, Perkin, Trans., 1887, **51**, 237), a substance was obtained which boiled at 136—137°, and, on analysis, gave numbers agreeing with the formula $C_6H_{10}O$. It smelt strongly of peppermint, combined readily with sodium hydrogen sulphite, and in general possessed properties which led the authors to the conclusion that it was tetramethylene methyl ketone. There can be doubt that this substance is identical with the product obtained by the action of tetramethylenecarboxylic chloride on zinc methide.

Tetramethylene methyl ketone is isomeric with methyldehydrohexone,  $\begin{array}{l} CH_3\cdot C—O—CH_2 \\ \quad\ \| \qquad\quad\ | \\ \quad CH\cdot CH_2\cdot CH_2 \end{array}$, which was obtained by the distillation of methyldehydrohexonecarboxylic acid (Trans., 1887, **51**, 723).

Tetramethylene Methyl Ketoxime,  $\begin{array}{l} CH_2\cdot CH_2 \\ |\qquad\ | \\ CH_2\cdot CH\cdot C(:NOH)\cdot CH_3 \end{array}$.

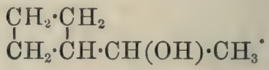
In order to obtain this substance, 5 grams of the pure ketone was dissolved in methyl alcohol, mixed with a solution of 13 grams of pure potassium hydrate in methyl alcohol, a concentrated aqueous solution of 5·3 grams of hydroxylamine hydrochloride added, and the whole allowed to stand for 15 hours. The product was mixed with water, the solution rendered slightly acid by the addition of hydrochloric acid, and extracted three times with ether; the ethereal solution was then washed with water, dried over calcium chloride, and the residual oily oxime purified by distillation under the ordinary pressure. Almost the whole distilled between 194° and 195° as a colourless oil, which solidified completely on standing for some days. The crystals were freed from traces of oily mother liquor by spreading on a porous plate, recrystallised from water, and the thick, colourless prisms thus obtained, after drying over sulphuric acid under reduced pressure, analysed with the following results :—

0·1166 gram substance gave 0·1064 gram H_2O and 0·2274 gram CO_2.
0·1309 gram substance gave 13·7 c.c. N; $t = 13°$; bar. = 755 mm.

	Theory. $C_6H_{11}NO$.	Found.
C	63·72 per cent.	63·71 per cent.
H.......	9·73 „	10·14 „
N	12·39 „	12·25 „

Tetramethylene methyl ketoxime melts at 60—61°, and possesses in a marked degree the odour characteristic of oximes. It is readily soluble in alcohol, benzene, light petroleum, and hot water, less so in cold water; it dissolves readily in concentrated hydrochloric acid, and in moderately concentrated sodium hydrate solution in the cold. If the solution in hot water is allowed to cool slowly, the ketoxime is gradually deposited in beautiful, colourless, six-sided prisms.

Tetramethylenemethylcarbinol,



$$\begin{array}{l}CH_2\cdot CH_2\\ |\qquad\ \ |\\ CH_2\cdot CH\cdot CH(OH)\cdot CH_3.\end{array}$$

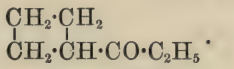
The reduction of tetramethylene methyl ketone to the corresponding secondary alcohol is readily accomplished by means of sodium in moist ethereal solution. 10 grams of the pure ketone was dissolved in 100 grams of pure ether; the solution floated on a strong solution of sodium hydrate, contained in a stout bottle fitted with a reflux condenser, and then a large excess of sodium gradually added, and small quantities of water from time to time, if necessary, the course of the reaction being moderated by cooling the bottle with a stream of water. The ethereal solution was separated, washed with a little very dilute hydrochloric acid, then with water, dried over potassium carbonate, evaporated, and the oily residue purified by fractional distillation. Almost the whole passed over between 140° and 150°, leaving only a very small residue of high boiling point in the retort; on redistillation, a colourless oil was obtained boiling constantly at 144—145°; this gave the following results on analysis :—

0·1942 gram substance gave 0·2142 gram H_2O and 0·5071 gram CO_2.

	Theory. $C_6H_{12}O$.	Found.
C	72·00 per cent.	71·78 per cent.
H	12·00 „	12·25 „
O	16·00 „	15·97 „

Tetramethylenemethylcarbinol is a colourless, mobile liquid, possessing a powerful odour strongly resembling that of menthol; it boils constantly at 144—145°.

Tetramethylene Ethyl Ketone,



$$\begin{array}{l} CH_2\cdot CH_2 \\ | \qquad\quad | \\ CH_2\cdot CH\cdot CO\cdot C_2H_5 \end{array}.$$

This ketone is readily produced by the action of tetramethylenecarboxylic chloride on zinc ethide, and as considerable quantities of it were required, numerous experiments were instituted with the object of working out a method of preparation which would give a good yield of the pure substance. Ultimately the following process was adopted:—

Into a large flask, filled with dry carbonic anhydride, about 100 grams of very carefully purified and thoroughly dry ether is placed; 30 grams of zinc ethide are added, and then 50 grams of tetramethylenecarboxylic chloride slowly dropped in from a dropping funnel. At first, scarcely any reaction appears to take place, and there is very little evolution of heat, but, on standing for a few minutes, the mixture rapidly becomes warm, and a very vigorous reaction sets in, so that it is necessary to watch, and now and then cool the flask under the tap, otherwise loss from boiling over may occur. As soon as the decomposition is at an end, water is cautiously added, the ethereal solution separated, evaporated, and the residual oil submitted to distillation in a current of steam. The distillate is extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the crude ketone fractionated.

In our first experiments, almost the whole of the ketone thus prepared boiled constantly at 153°, and gave the following results on analysis:—

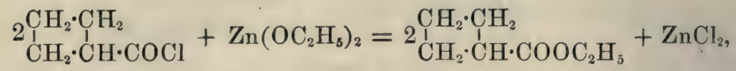
I. 0·2036 gram substance gave 0·1860 gram H_2O and 0·5300 gram CO_2.

II. 0·1026 gram substance gave 0·0954 gram H_2O and 0·2672 gram CO_2.

	Theory. $C_7H_{14}O$.	Found. I.	Found. II.
C	75·00 per cent.	70·99	71·02 per cent.
H	10·72 ,,	10·14	10·33 ,,
O	14·28 ,,	18·87	18·65 ,,

These analyses differ from theory by a minus of 4 per cent. of carbon and 0·5 per cent. of hydrogen, and for a long time no explanation of this curious discrepancy was forthcoming.

Ultimately it was discovered that the liquid was a a mixture containing considerable quantities of ethyl tetramethylenecarboxylate, the formation of which must be due to the action of tetramethylenecarboxylic chloride on zinc ethylate contained in the zinc ethide employed, thus:—



$$2\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ | \qquad | \\ \mathrm{CH_2\cdot CH\cdot COCl}\end{matrix} + \mathrm{Zn(OC_2H_5)_2} = 2\begin{matrix}\mathrm{CH_2\cdot CH_2}\\ | \qquad | \\ \mathrm{CH_2\cdot CH\cdot COOC_2H_5}\end{matrix} + \mathrm{ZnCl_2},$$

and as this ethereal salt boils at approximately the same temperature as the ketone, a separation by fractional distillation was out of the question. In order to obtain the pure ketone from this mixture, the oil was digested with an excess of alcoholic potash for one hour in a flask connected with a reflux apparatus, the product mixed with water, distilled with steam, the distillate extracted with pure ether, the ethereal solution dried over calcium chloride, evaporated, and the colourless, oily residue purified by fractionation.

During the first distillation, almost the whole passed over between 154° and 157°, leaving only a very small residue in the retort, and on repeated fractionation, a colourless oil was obtained boiling constantly at 155—156°; this, on analysis, gave the following results:—

0·1529 gram substance gave 0·1528 gram H_2O and 0·4199 gram CO_2.

	Theory. $C_7H_{12}O$.	Found.
C	75·00 per cent.	74·89 per cent.
H	10·72 ,,	11·10 ,,
O.......	14·28 ,,	14·01 ,,

Tetramethylene ethyl ketone is a colourless, mobile oil, smelling strongly of peppermint. It boils at 155—156°, and is less soluble in water than the corresponding methyl ketone.

A vapour density determination of this substance, made by Hofmann's method in a vacuum, at the temperature of boiling aniline, gave—

			Theory. $C_7H_{14}O$.
D........	3·6	D........	3·8

The density and magnetic rotation determinations of tetramethylene ethyl ketone gave the following results:—

Density.—*d* 4°/4° = 0·9094; *d* 5°/5° = 0·9086; *d* 10/°10° = 0·9044; *d* 15°/15° = 0·9004; *d* 20°/20° = 0·8970; *d* 25°/25° = 0·8934.

Magnetic Rotations.

	t.	Sp. rotation.	Mol. rotation.
	17·0°	1·0052	6·963
	17·0	0·9990	6·922
	17·0	1·0012	6·936
	19·0	0·9988	6·923
	19·0	0·9988	6·923
	19·0	0·9921	6·877
	19·0	0·9861	6·836
Average ..	18·1	0·9972	6·911

As in the case of tetramethylene methyl ketone, this ketone has a rotation *lower* than the nearest corresponding saturated ketone which has been examined (butyrone). Thus—

Magnetic rotation of butyrone	7·489
Less H_2 for difference in composition	0·508
	6·981
Tetramethylene ethyl ketone	6·911
Difference	0·070

Sodium Hydrogen Sulphite Compound of Tetramethylene Ethyl Ketone, $C_7H_{14}O,NaHSO_3$.

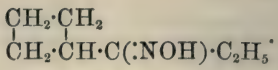
When shaken with a concentrated solution of sodium hydrogen sulphite containing a large excess of sulphurous anhydride, tetramethylene ethyl ketone gradually dissolved, and the solution, on standing, slowly deposited beautiful, glistening prisms. These were collected, washed with water, dried first on a porous plate and then over sulphuric acid, and analysed with the following result :—

0·1498 gram substance, heated with sulphuric acid, gave 0·0518 gram Na_2SO_4.

	Theory. $C_7H_{12}O,NaHSO_3$.	Found.
Na	10·65 per cent.	11·18 per cent.

This substance is moderately soluble in water ; when warmed with dilute sulphuric acid, or with sodium carbonate solution, it is decomposed, with separation of an oil, which is obviously the regenerated ketone. Grimm (*Annalen*, **157**, 262) states that only methyl ketones combine with sodium hydrogen sulphite. Tetramethylene ethyl ketone is an exception to this rule.

Tetramethylene Ethyl Ketoxime,



$$\begin{array}{l} CH_2\cdot CH_2 \\ CH_2\cdot CH\cdot C(:NOH)\cdot C_2H_5 \end{array}.$$

In preparing this oxime, 7 grams of the pure ketone was dissolved in a solution of 15 grams of pure potassium hydrate in methyl alcohol, 6 grams of hydroxylamine hydrochloride dissolved in the smallest possible quantity of water added, and the whole allowed to stand for 15 hours. The product was mixed with water, rendered slightly acid by the addition of hydrochloric acid, extracted three times with ether, the ethereal solution washed with water, dried over calcium chloride, evaporated, and the residual oil purified by fractionation.

Tetramethylene ethyl ketoxime is a thick, colourless oil boiling constantly at 208—209° (750 mm.); it does not solidify even on long standing. It dissolves easily in hydrochloric acid, and, on warming, the solution is rapidly decomposed with regeneration of the ketone.

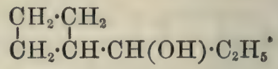
A carefully purified sample of this oxime gave the following results on analysis:—

0·1248 gram substance gave 0·1178 gram H_2O and 0·3011 gram CO_2.

0·1369 gram substance gave 13·3 c.c. N; t = 15·5°; bar. = 748 mm.

	Theory. $C_7H_{13}NO$.	Found.
C	66·14 per cent.	65·97 per cent.
H	10·24 ,,	10·48 ,,
N	11·02 ,,	11·15 ,,

Tetramethyleneethylcarbinol,



$$\begin{array}{l} CH_2\cdot CH_2 \\ CH_2\cdot CH\cdot CH(OH)\cdot C_2H_5 \end{array}.$$

In order to prepare this secondary alcohol, we experimented in the first place on the action of sodium amalgam on the dilute alcoholic solution of tetramethylene ethyl ketone; 29 grams of the pure ketone was dissolved in 80 grams of alcohol, water was then added until a very faint turbidity was produced, and the solution treated with 1200 grams of 2½ per cent. sodium amalgam, in quantities of about 200 grams at a time, the ketone being kept in solution, and the reaction promoted by the occasional addition of dilute alcohol. As soon as the amalgam had been completely decomposed, the whole was mixed with water, the mercury run off, and the solution extracted several times with ether. After washing with water, drying over potassium carbonate, and evaporating the ethereal solution, a colourless oil was left which boiled constantly at 155—156°, and, on analysis, gave numbers agreeing with the formula $C_7H_{12}O$, showing that no reduction had taken place, and in fact almost the whole of the ketone was recovered unchanged.

After this curious result, no further experiments were made on the action of sodium amalgam on tetramethylene ethyl ketone, as it was found that it could be reduced to the carbinol with great ease by means of sodium in moist ethereal solution.

24 grams of the pure ketone was dissolved in about 300 c.c. of pure ether, the ethereal solution floated on water, and treated with a large excess of sodium, the operation being conducted exactly as described under tetramethylenemethylcarbinol (p. 50). During the reduction, a considerable quantity of a white sodium compound separated, which was probably the sodium compound of the carbinol; this was readily decomposed by the addition of water. As soon as the last traces of the sodium had disappeared, the ethereal solution was separated, washed with very dilute hydrochloric acid, dried over anhydrous potassium carbonate, evaporated, and the almost colourless residue distilled under reduced pressure. Almost the whole of it passed over at 120° (290 mm.), leaving only a very slight residue in the retort, and this fraction, on subsequent distillation under ordinary pressures, boiled constantly at 162° (754 mm.); the yield obtained was fully 20 grams.

The substance was once more fractioned, and then analysed with the following result:—

0·1183 gram substance gave 0·1320 gram H_2O and 0·3189 gram CO_2.

	Theory. $C_7H_{14}O$.	Found.
C.......	73·68 per cent.	73·52 per cent.
H.......	12·27 „	12·39 „
O.......	14·05 „	14·09 „

Tetramethyleneethylcarbinol is a colourless oil of agreeable odour, sparingly soluble in water. It boils constantly at 162°. The density and magnetic rotation determinations gave the following results:—

Density.—*d* 4°/4° = 0·9092; *d* 5°/5° = 0·9083; *d* 10°/10° = 0·9044; *d* 15°/15° = 0·9007; *d* 20°/20° = 0·8974; *d* 25°/25° = 0·8945.

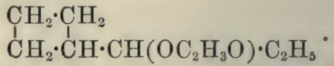
Magnetic Rotations.

t.	Sp. rotation.	Mol. rotation.
18·4°	1·0384	7·319
18·4	1·0445	7·368
18·4	1·0394	7·327
18·4	1·0363	7·303
19·0	1·0347	7·297
19·0	1·0371	7·317
19·0	1·0378	7·321
19·0	1·0378	7·321
20·0	1·0386	7·329
20·0	1·0377	7·322
20·0	1·0407	7·346
Average 18·8	1·0384	7·325

On examining these numbers, it will be seen that the relation between tetramethylene ethyl ketone and tetramethyleneethylcarbinol is very similar to that between a ketone and a secondary alcohol in the fatty series, thus:—

Magnetic rotation of isopropyl alcohol	4·019
,, ,, acetone	3·514
Difference	0·505
Magnetic rotation of tetramethyleneethylcarbinol...	7·325
,, ,, tetramethylene ethyl ketone ..	6·911
Difference	0·414

Tetramethyleneethylcarbinyl Acetate,



$$\begin{array}{l} CH_2\cdot CH_2 \\ |\qquad\ \ | \\ CH_2\cdot CH\cdot CH(OC_2H_3O)\cdot C_2H_5 \end{array}$$

In order to prepare this acetate, 5 grams of the pure carbinol was digested with 15 grams of acetic anhydride for 15 minutes, the product distilled, and then very carefully fractionated, in order to separate the acetate as completely as possible from unchanged acetic anhydride. After four fractionations, a colourless oil was obtained which boiled constantly at 178—179°, and gave the following results on analysis:—

0·1158 gram substance gave 0·1071 gram H_2O and 0·2912 gram CO_2.

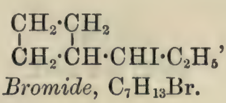
	Theory. $C_9H_{16}O_2$.	Found.
C	69·23 per cent.	68·58 per cent.
H	10·26 ,,	10·27 ,,
O	20·51 ,,	21·15 ,,

Tetramethyleneethylcarbinyl acetate is a colourless oil possessing the odour characteristic of the acetates of the higher alcohols of the fatty series; it is readily hydrolysed by boiling with aqueous potassium hydrate solution. A quantitative experiment was made in order to determine the amount of acetic acid produced by the hydrolysis.

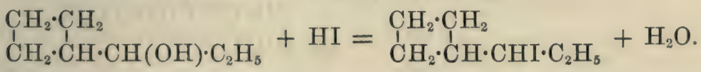
1·2511 grams of the substance was boiled in a reflux apparatus with 150 c.c. of standard potassium hydrate solution for six hours, allowed to cool, and the solution neutralised by the addition of standard sulphuric acid solution.

83·1 c.c. of potassium hydrate solution (1 c.c. = 0·00559 gram KOH) had been neutralised during the hydrolysis; this corresponds to 39·65 per cent. acetic acid, whereas $C_9H_{16}O_2$ should yield on hydrolysis 38·46 per cent. acetic acid.

This result shows that, in spite of careful fractionation, the acetate probably still contained traces of acetic anhydride; this would account for the slight deficiency of carbon found in the elementary analysis.

Tetramethylenepropyl Iodide,  $\begin{array}{l}CH_2\cdot CH_2\\ |\qquad\ \ |\\ CH_2\cdot CH\cdot CHI\cdot C_2H_5\end{array}$, *and Tetramethylenepropyl Bromide,* $C_7H_{13}Br$.

Tetramethyleneethylcarbinol readily reacts with hydriodic acid with formation of tetramethylenepropyl iodide, thus:—



$$\begin{array}{l}CH_2\cdot CH_2\\ |\qquad\ \ |\\ CH_2\cdot CH\cdot CH(OH)\cdot C_2H_5\end{array} + HI = \begin{array}{l}CH_2\cdot CH_2\\ |\qquad\ \ |\\ CH_2\cdot CH\cdot CHI\cdot C_2H_5\end{array} + H_2O.$$

7·5 grams of the pure carbinol was shaken with 40 grams of fuming hydriodic acid (sp. gr. 1·96); the mixture, which became very warm, allowed to stand over night, and then heated to boiling in a flask connected with a reflux apparatus for a few minutes. The product was poured into water, extracted twice with ether, the ethereal solution washed well with water containing a little sulphurous anhydride, dried over calcium chloride, evaporated, and the slightly brownish, oily residue purified by fractionation under reduced pressure. In this way, a colourless oil was obtained which boiled constantly at 105—107° (80 mm.), and gave the following results on analysis:—

0·2915 gram substance gave 0·2998 gram AgI.

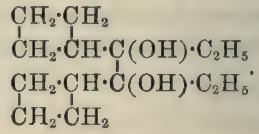
	Theory. $C_7H_{13}I$.	Found.
I.........	56·69 per cent.	55·62 per cent.

Tetramethylenepropyl iodide is a heavy, colourless oil, which possesses an odour strongly resembling that of hexyl iodide. When pure, it may be distilled in small quantities under ordinary pressures with only slight decomposition, but the crude substance cannot be purified by fractionation except under greatly reduced pressure, and even then slight decomposition seems to take place, as indicated by the above analysis. The pure iodide soon turns brown on exposure to light. It is rapidly decomposed by boiling with water with formation of hydriodic acid. When heated in a sealed tube with fuming hydriodic acid and amorphous phosphorus at 230°, it is readily reduced with formation of a hydrocarbon, which is at present under investigation.

Tetramethylenepropyl bromide, $C_7H_{13}Br$, is similarly produced by the action of hydrobromic acid (sp. gr. 1·83) on tetramethyleneethylcarbinol. It is a colourless oil, which has an odour closely resembling that of trimethylene bromide; it boils constantly at 110° (120 mm.). Analysis:—

0·2336 gram substance gave 0·2430 gram AgBr.

	Theory. $C_7H_{13}Br$.	Found.
Br......	45·20 per cent.	44·51 per cent.

Ditetramethylene Diethyl Glycol, 

$$\begin{array}{l} CH_2\cdot CH_2 \\ |\qquad\ | \\ CH_2\cdot CH\cdot C(OH)\cdot C_2H_5 \\ \qquad\qquad\ \ | \\ CH_2\cdot CH\cdot C(OH)\cdot C_2H_5 \\ |\qquad\ | \\ CH_2\cdot CH_2 \end{array}.$$

Two experiments on the reduction of tetramethylene ethyl ketone in moist ethereal solution by means of sodium were made; in the first, an almost quantitative yield of tetramethyleneethylcarbinol was obtained; whilst in the second, conducted apparently under precisely similar conditions, a comparatively small quantity of the carbinol was produced, and the product, on distillation under reduced pressure, gave a considerable fraction boiling at 220—223° (100 mm.), which, on standing, almost completely solidified. The crystals were spread on a porous plate until free from oily mother liquor, dried over sulphuric acid, and analysed (I). The substance was then purified by recrystallisation from light petroleum and again analysed (II).

I. 0·1392 gram substance gave 0·1447 gram H_2O and 0·3790 gram CO_2.

II. 0·1525 gram substance gave 0·1596 gram H_2O and 0·4155 gram CO_2.

	Theory. $C_{14}H_{26}O_2$.	Found. I.	Found. II.
C	74·34 per cent.	74·26	74·31 per cent.
H	11·50 ,,	11·55	11·41 ,,
O	14·16 ,,	14·19	14·28 ,,

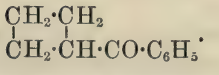
The molecular weight was determined by Raoult's method, using acetic acid as the solvent, with the following results :—

Weight of substance taken	0·4643 gram.
Weight of acetic acid taken	24·35 grams.
Melting point of the acetic acid	16·19°
,, ,, mixture..........	15·87°
Depression of the melting point........	0·32°
Molecular weight, $C_{14}H_{26}O_2$	226
Found	232

This substance is, therefore, ditetramethylene diethyl glycol, the pinacone derived from tetramethylene ethyl ketone.

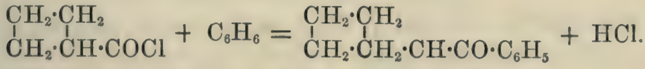
It melts at 95°, and, when liquid, smells strongly of peppermint; it is very readily soluble in alcohol, benzene, and warm light petroleum, sparingly in water; on slowly cooling its solution in warm light petroleum, it crystallises in curiously striated masses consisting of transparent, colourless prisms usually radiating from a centre.

Tetramethylene Phenyl Ketone,



$$\begin{matrix} CH_2\cdot CH_2 \\ | \quad\ \ | \\ CH_2\cdot CH\cdot CO\cdot C_6H_5 \end{matrix}.$$

This interesting compound is produced when a solution of tetramethylenecarboxylic chloride in excess of benzene is treated with aluminium chloride:



$$\begin{matrix} CH_2\cdot CH_2 \\ | \quad\ \ | \\ CH_2\cdot CH\cdot COCl \end{matrix} + C_6H_6 = \begin{matrix} CH_2\cdot CH_2 \\ | \quad\ \ | \\ CH_2\cdot CH_2\cdot CH\cdot CO\cdot C_6H_5 \end{matrix} + HCl.$$

The following method, which has been repeatedly employed, gives a good yield of tetramethylene phenyl ketone :—

40 grams of pure aluminium chloride and 100 grams of pure, dry benzene (free from thiophen) are mixed in a large flask, and then a solution of 30 grams of tetramethylenecarboxylic chloride in 60 grams of benzene slowly added through a dropping funnel. During the operation, the mixture becomes slightly warm, and some hydrogen chloride is evolved; the product, after standing for 15 minutes, is heated to boiling in a reflux apparatus by means of a water-bath for half an hour, well cooled, and gradually mixed with

water containing some hydrochloric acid. The upper benzene layer is separated, washed with water containing a little sodium carbonate, dried over calcium chloride, the benzene distilled off, and the residual crude, dark-coloured ketone distilled under reduced pressure. About 22 grams of a colourless oil boiling at 180—200° (150 mm.) are obtained, and this, on fractionation under ordinary pressures, distils almost entirely between 258° and 259° (740 mm.).

The analysis of this substance gave the following numbers :—

0·1280 gram substance gave 0·0874 gram H_2O and 0·3859 gram CO_2.

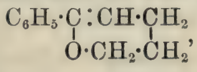
	Theory. $C_{11}H_{12}O$.	Found.
C	82·50 per cent.	82·22 per cent.
H	7·50 ,,	7·59 ,,
O	10·00 ,,	10·21 ,,

The molecular weight was determined by Raoult's method, using acetic acid as the solvent, with the following results :—

Weight of substance taken	0·9368 gram
,, acetic acid taken	50·85 grams
Melting point of the acetic acid......	15·009°
,, ,, mixture........	14·590°
Depression of the melting point......	0·419°
Molecular weight, $C_{11}H_{12}O$	160
Found............................	170

Tetramethylene phenyl ketone is a thick, colourless oil which boils without decomposition at 258—259°, but, on standing, soon acquires a slight yellowish tinge; it has an odour which can scarcely be distinguished from that of butyl phenyl ketone,

$$C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$$

(b. p. 236—238° at 720 mm.). It is isomeric with phenyldehydrohexone,  $\begin{array}{l} C_6H_5\cdot C : CH\cdot CH_2 \\ \quad\ \ | \qquad\quad | \\ \quad\ O\cdot CH_2\cdot CH_2 \end{array}$, which boils at 249—251° (Trans., 1887, **51**, 731).

The density and magnetic rotation determinations of this substance gave the following results :—

Density.—$d\,4°/4° = 1·0600$; $d\,5°/5° = 1·0591$; $d\,10°/10° = 1·0551$; $d\,15°/15° = 1·0515$; $d\,20°/20° = 1·0485$; $d\,25°/25° = 1·0457$.

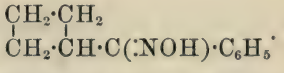
Magnetic Rotation.

t.	Sp. rotation.	Mol. rotation.
16·5°	1·8234	15·431
16·5	1·8300	15·485
16·5	1·8345	15·523
16·5	1·8330	15·510
18·5	1·8260	15·469
18·5	1·8266	15·474
18·5	1·8314	15·515
18·5	1·8230	15·443
19·5	1·8160	15·391
19·5	1·8136	15·371
19·5	1·8226	15·448
Average 18·0	1·8255	15·460

The magnetic rotation of tetramethylene phenyl ketone may be calculated from that of the corresponding ethyl ketone, thus :—

Magnetic rotation of tetramethylene ethyl ketone..	6·911
— the value of C_2H_4	2·046
	4·865
+ the value of C_6H_5 replacing hydrogen....	10·406
Calculated magnetic rotation of tetramethylene phenyl ketone	15·271
This number agrees well with that actually found, namely	15·460

Tetramethylene Phenyl Ketoxime,



$$\begin{array}{l} CH_2{\cdot}CH_2 \\ CH_2{\cdot}CH{\cdot}C(:NOH){\cdot}C_6H_5 \end{array}$$

In order to prepare this substance, 5 grams of the pure ketone was dissolved in methyl alcohol, mixed with a solution of 8 grams of potassium hydrate dissolved in methyl alcohol, a concentrated aqueous solution of 3·3 grams of hydroxylamine hydrochloride added, and the mixture allowed to stand for 15 hours. On diluting the product with water, the oxime separated in colourless needles; these were extracted with ether, the ethereal solution washed with water, dried over calcium chloride, evaporated, and the solid residue purified by recrystallisation from 80 per cent. alcohol. The beautiful, colourless needles thus obtained, after drying over sulphuric acid under reduced pressure, gave the following numbers on analysis :—

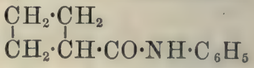
0·1207 gram substance gave 0·0832 gram H_2O and 0·3322 gram CO_2.

0·1944 gram substance gave 12·9 c.c. N; $t = 9·5°$; bar. = 758 mm.

	Theory. $C_{11}H_{13}NO$.	Found.
C......	75·42 per cent.	75·10 per cent.
H......	7·42 ,,	7·66 ,,
N......	8·00 ,,	7·93 ,,

Tetramethylene phenyl ketoxime melts at 91—93°. It is readily soluble in benzene and alcohol, but only sparingly in cold light petroleum, and almost insoluble in water. It dissolves readily in strong hydrochloric acid in the cold, and in warm, dilute potassium hydrate solution. It crystallises from dilute alcohol in colourless needles, and from light petroleum in long, thin, slender needles.

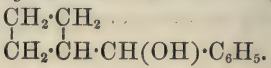
The oxime dissolves very readily in acetyl chloride with slight evolution of heat; on distilling off the acetyl chloride and heating the residue, a very violent reaction sets in, the original colourless liquid becoming quite brown. If the semi-solid residue is distilled with concentrated potassium hydrate solution, a strong odour of aniline is noticeable, and it appears probable that in the above reaction the oxime undergoes intramolecular change, with formation of the anilide of tetramethylenecarboxylic acid,



$$\begin{array}{l} CH_2\cdot CH_2 \\ \,|\qquad\;\; | \\ CH_2\cdot CH\cdot CO\cdot NH\cdot C_6H_5 \end{array}$$

This point is being further investigated.

Reduction of Tetramethylene Phenyl Ketone. Formation of Tetramethylenephenylcarbinol,



$$\begin{array}{l} CH_2\cdot CH_2 \\ \,|\qquad\;\; | \\ CH_2\cdot CH\cdot CH(OH)\cdot C_6H_5. \end{array}$$

This reduction was conducted exactly as in the case of the reduction of the corresponding ethyl and methyl ketones. 36 grams of tetramethylene phenyl ketone was dissolved in ether, the solution floated on water, and treated with 40 grams of sodium; the ethereal solution was then washed with water containing a little hydrochloric acid, allowed to stand for about 24 hours, until no more crystals of ditetramethylene diphenyl glycol separated (p. 66), filtered, dried over potassium carbonate, evaporated, and the residual oil purified by fractionation under reduced pressure. In this way a colourless oil (21 grams) was obtained boiling constantly at 180° (100 mm.), but there was a considerable residue in the retort, which will be referred to later on. The analysis of the substance boiling at 180° (100 mm.) gave the following results:—

I. 0·1679 gram substance gave 0·1412 gram H_2O and 0·4979 gram CO_2.

II. 0·1409 gram substance gave 0·1188 gram H_2O and 0·4188 gram CO_2.

	Theory. $C_{11}H_{14}O$.	Found. I.	Found. II.
C......	81·48 per cent.	80·87	81·06 per cent.
H......	8·64 ,,	9·34	9·36 ,,
O......	9·88 ,,	9·79	9·58 ,,

The product was then refractioned at ordinary pressures, when, almost the whole passed over at 257° (752 mm.), and, on analysis, gave the following results:—

I. 0·1111 gram substance gave 0·0942 gram H_2O and 0·3299 gram CO_2.

II. 0·1734 gram substance gave 0·1436 gram H_2O and 0·5123 gram CO_2.

	Found. I.	Found. II.
C............	80·98	80·57 per cent.
H............	9·42	9·20 ,,
O............	9·60	9·23 ,,

The refractionation had not materially altered the composition of the substance. It will be seen that this alcohol contains considerably more hydrogen than is required by the formula $C_{11}H_{14}O$, and this very curious result can only be explained on the assumption that during the reduction the benzene ring has been partially reduced. This is borne out by the results obtained in the determination of the magnetic rotation of this preparation.

Density.—*d* 4°/4° = 1·0309; *d* 5°/5° = 1·0301; *d* 10°/10° = 1·0265; *d* 15°/15° = 1·0231; *d* 20°/20° = 1·0201; *d* 25°/25° = 1·0175.

Magnetic Rotations.

t.	Sp. rotation.	Mol. rotation.
14·0°	1·7043	14·982
14·0	1·6932	14·884
14·0	1·6979	14·926
14·0	1·6964	14·913
16·37°	1·6848	14·833
16·37	1·6926	14·901
16·37	1·6915	14·892
16·37	1·6859	14·842
16·37	1·6903	14·881
Average 15·31	1·6930	14·895

The effect of reducing tetramethylene ethyl ketone to the corresponding carbinol is to raise the magnetic rotation by 0·414; and as the reduction of tetramethylene phenyl ketone proceeds on exactly the same lines, the magnetic rotation of tetramethylenephenylcarbinol may be calculated thus:—

Magnetic rotation of tetramethylene phenyl ketone	15·460
+ the effect produced by adding H_2 to the carbonyl group	0·414
Calculated rotation of tetramethylenephenylcarbinol	15·874
Result obtained in the above experiments	14·895
Deficiency	0·979

As benzene has an abnormally high rotation, the saturated hydrocarbons, on the other hand, a low rotation, the above deficiency may be easily accounted for on the assumption that the substance contains a compound in which the benzene ring has been partially reduced. Experiments on the action of sodium in moist ethereal solution on other benzene derivatives, such as acetophenone, have given results which clearly indicate that in these cases also the benzene ring is partially reduced, although the derivatives obtained have not yet been obtained in a pure condition (compare also Perkin and Schloesser, Trans., 1890, **57**, 955).

In order to obtain pure tetramethylenephenylcarbinol, the experiments on the reduction of the ketone in moist ethereal solution were repeated on a smaller scale, twice the quantity of sodium (for H_2) being employed. In this way a colourless oil was obtained which distilled at 257—259° (750 mm.), and gave the following results on analysis:—

0·1550 gram substance gave 0·1240 gram H_2O and 0·4621 gram CO_2.

	Theory. $C_{11}H_{14}O$.	Found.
C	81·48 per cent.	81·31 per cent.
H	8·64 ,,	8·89 ,,
O	9·88 ,,	9·80 ,,

Tetramethylenephenylcarbinol is a thick, colourless oil, possessing an odour closely resembling that of phenylmethylcarbinol, although not quite so pronounced. It is sparingly soluble in water; it does not dissolve in, but it reacts readily with, concentrated aqueous solutions of hydrobromic and hydriodic acids, forming heavy oils, which are probably the corresponding bromide and iodide of benzyltetramethylene.

Polymeride of Tetramethylenephenylcarbinol.—In fractioning the crude product of the reduction of tetramethylene phenyl ketone, a thick, yellow substance boiling above 190° (100 mm.) was always left in the flask. The small quantities obtained from several operations were collected and rapidly distilled from a small fractionating flask under a pressure of 60 mm., and the thick oil which boiled almost constantly at 320° analysed with the following result:—

0·1062 gram substance gave 0·0882 gram H_2O and 0·3159 gram CO_2.

	Theory. $C_{22}H_{28}O_2$.	Found.
C	81·48 per cent.	81·12 per cent.
H	8·64 ,,	9·22 ,,
O	9·88 ,,	9·66 ,,

The determination of the molecular weight by Raoult's method, using acetic acid as the solvent, gave the following results:—

Weight of substance taken...............	1·2644 grams.
Weight of acetic acid taken.............	31·68 grams.
Melting point of the acetic acid..........	16·14°
Melting point of the mixture............	15·625°
Depression of the melting point..........	0·515°
Molecular weight, $C_{22}H_{28}O_2$..............	322
Found	302

This substance has, therefore, the formula $C_{22}H_{28}O_2$, and must be looked upon as a polymeride of tetramethylenephenylcarbinol containing 2 mols. of this carbinol, thus:—

$$C_{22}H_{28}O_2 = 2C_{11}H_{14}O.$$

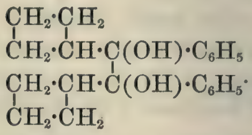
When it is slowly distilled under a pressure of 100 mm., it is gradually decomposed, and on repeating the operation several times, a large quantity of an oil of comparatively low boiling point is obtained; this, on fractionation under ordinary pressures, boils constantly at 256—257°, and consists of pure tetramethylenephenylcarbinol, as the following analysis shows:—

0·1150 gram substance gave 0·0879 gram H_2O and 0·3440 gram CO_2.

	Theory. $C_{11}H_{14}O$.	Found.
C......	81·48 per cent.	81·40 per cent.
H......	8·64 ,,	8·47 ,,
O......	9·88 ,,	10·13 ,,

If the distillation is repeated sufficiently often, it appears that the whole of this polymeride may in this way be converted into pure tetramethylenephenylcarbinol.

Ditetramethylene Diphenyl Glycol,



When the ethereal solution of the reduction products of tetramethylenephenylcarbinol (see preceding section) was allowed to stand for about 24 hours, a white, crystalline substance separated; this was collected, well washed with ether, recrystallised from this solvent, and analysed with the following results:—

I. 0·1390 gram substance gave 0·1026 gram H_2O and 0·4180 gram CO_2.

II. 0·1740 gram substance gave 0·1282 gram H_2O and 0·5225 gram CO_2.

III. 0·1884 gram substance gave 0·1398 gram H_2O and 0·5613 gram CO_2.

	Theory. $C_{22}H_{26}O_2$.	Found. I.	II.	III.
C	81·98 per cent.	82·04	81·90	81·29 per cent.
H	8·08 ,,	8·20	8·18	8·24 ,,
O	9·94 ,,	9·76	9·92	10·47 ,,

The molecular weight was determined by Raoult's method, using acetic acid as the solvent, with the following results:—

Weight of substance taken	0·5839 gram.
Weight of acetic acid taken......	28·5 grams.
Melting point of the acetic acid...	16·19°
,, ,, mixture	15·95°
Depression of the melting point ..	0·24°
Molecular weight, $C_{22}H_{26}O_2$.......	322
Found	333

This substance has therefore the formula $C_{22}H_{26}O_2$, and is obviously the pinacone of tetramethylene phenyl ketone.

Ditetramethylene diphenyl glycol melts at 153—154°. It dissolves readily in boiling glacial acetic acid and toluene, moderately easily in boiling alcohol, but only sparingly in ether and light petroleum. On slowly cooling its solution in boiling glacial acetic acid, it crystallises in long, colourless needles grouped together in parallel bundles.

IV.—CONTRIBUTIONS FROM THE LABORATORIES OF THE HERIOT WATT COLLEGE, EDINBURGH.

The Synthetical Formation of Closed Carbon Chains. Part I (continued). *Action of Propylene Bromide on the Sodium Compounds of Ethyl Acetoacetate and Ethyl Benzoylacetate.*

By W. H. Perkin, Jun., Ph.D., F.R.S., and James Stenhouse.

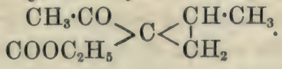
The action of ethylene bromide on the sodium compounds of ethyl malonate, ethyl acetoacetate, and ethyl benzoylacetate has been made the subject of repeated investigation (Fittig, Roeder, *Ber.*, **16**, 372. Perkin, *Ber.*, **17**, 54; Trans., 1885, **47**, 801; 1887, **51**, 849. Freer and Perkin, Trans., 1887, **51**, 820. Colman and Perkin, Trans., 1889, **55**, 358. Marshall and Perkin, Trans., 1891, **59**, 853. Lipp, *Ber.*, **22**, 1210), and the results obtained in these researches have led to the conclusion that in all these cases trimethylene derivatives are formed.

During the course of these investigations, we have been carrying on parallel experiments on the action of propylene bromide on the sodium compounds of ethyl acetoacetate and ethyl benzoylacetate. Propylene bromide does not react with these compounds nearly so readily as ethylene bromide, and the result is that the yields obtained are exceedingly small; we have, therefore, in one or two cases, not been able to examine the products as fully as could have been desired.

The investigation of the products has, however, proved that, in every case, substances are found which have a constitution analogous to those obtained when ethylene bromide is employed.

The Action of Propylene Bromide on the Sodium Compound of Ethyl Acetoacetate.

Ethyl Acetylmethyltrimethylenecarboxylate [1, 2, 1],



$$\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\!>\!C\!<\!\begin{matrix}CH\cdot CH_3\\ |\\ CH_2\end{matrix}.$$

A short account of this reaction, and of some of the products obtained, has already been published (Trans., 1885, **47**, 850).

In the present instance, the quantities employed in one operation were the following:—

Ethyl acetoacetate	208 grams.
Sodium	36·8 grams.
Absolute alcohol	450 grams.
Propylene bromide	160 ,,

The sodium was dissolved in the alcohol, the well-cooled solution of sodium ethylate thus obtained gradually mixed with the ethyl acetoacetate, care being taken to prevent any appreciable rise of temperature by cooling with water; the propylene bromide was then added, and the mixture transferred to soda-water bottles, and heated at 100° for six hours. The alcoholic solution was decanted from the cake of sodium bromide which had formed, the alcohol distilled off on a water-bath, the residue mixed with water and the washings from the soda-water bottles, and extracted four times with ether. The ethereal solution was well washed with water containing a few drops of hydrochloric acid, dried over calcium chloride, evaporated, and the residual thick oil, which weighed about 100 grams, submitted to fractional distillation.

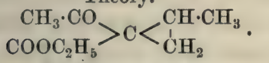
Between 125° and 160° (A), a large quantity of a heavy, colourless oil, which weighed about 54 grams, and consisted for the most part of unchanged propylene bromide, passed over. The thermometer then rose rapidly to 190° (B), and the residue, on fractionation under reduced pressure (100 mm.), distilled almost entirely between 130° and 260° (C), leaving a dark-brown residue in the retort; this, on cooling, partially solidified, and consisted of impure dehydracetic acid. The fraction below 125°, which smelt strongly of ethyl acetate, was repeatedly distilled, as it appeared probable that this fraction might contain α- or β-bromopropylene, C_3H_5Br, but as the portion boiling at 45—65° did not decolorise bromine, it is evident that these substances are not formed in any appreciable quantity in this reaction.

The fraction 125—160° (A) was twice fractioned, and the portion boiling between 130° and 150°, and which consisted for the most part of propylene bromide, was employed in the decomposition of fresh quantities of ethyl acetoacetate. It should be mentioned that a quantity of propylene bromide passes over with the alcohol, when the crude product of the reaction is distilled from a water-bath as described above. This is easily recovered by diluting the alcoholic distillate with twice its volume of water, allowing the milky liquid to stand till clear, and then separating the heavy layer of propylene bromide.

The fraction 130—230° (C) was distilled under the ordinary pressure, all passing over below 240° (D) being collected, and the residue (E) reserved for subsequent treatment.

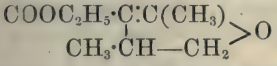
The fraction D was mixed with the fraction B, and submitted to repeated fractionation from a Würtz flask provided with a long neck; in this way it was approximately separated into crude ethyl acetoacetate (b. p. 175—190°) and crude ethyl acetylmethyltrimethylenecarboxylate (b. p. 190—225°). The latter fraction was again repeatedly distilled, and a small quantity of a colourless oil which boiled fairly constantly at 210—212° analysed with the following result:—

0·1611 gram substance gave 0·1215 gram H_2O and 0·3725 gram CO_2.


$\begin{array}{l}CH_3\cdot CO\\ COOC_2H_5\end{array}>C<\begin{array}{l}CH\cdot CH_3\\ |\\ CH_2\end{array}$.

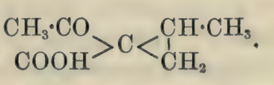
	Theory.	Found.	Previous analysis.
C . . .	63·53 per cent.	63·06 per cent.	63·55 per cent.
H	8·24 ,,	8·38 ,,	8·42 ,,
O	28·23 ,,	28·56 ,,	28·03 ,,

The substance employed in the previous analysis boiled at 215—217° (720 mm.); and there can be no doubt that the product boiling about 215° consists of nearly pure ethyl acetylmethyltrimethylenecarboxylate, the difference in the boiling point observed in the several preparations being probably due to the substance containing varying quantities of the isomeric ethyl dimethyldehydropentonecarboxylate,


$\begin{array}{l}COOC_2H_5\cdot C{:}C(CH_3)\\ \quad\;\; |\\ \quad CH_3\cdot CH—CH_2\end{array}>O$; the composition of this oil being apparently very similar to that obtained in the action of ethylene bromide on the sodium compound of ethyl aceteoacetate, which has been proved to be a mixture of ethyl acetyltrimethylenecarboxylate and ethyl methyldehydropentonecarboxylate.

The yield of the ethereal salt obtained by the above method is very small, not more than 50 grams of the fraction 205—215° being produced from 1 kilo. of ethyl acetoacetate.

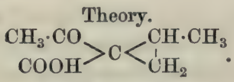
Acetylmethyltrimethylenecarboxylic Acid,


$\begin{array}{l}CH_3\cdot CO\\ COOH\end{array}>C<\begin{array}{l}CH\cdot CH_3\\ |\\ CH_2\end{array}$.

This acid has been previously described and analysed (Trans., 1885, **47**, 851).

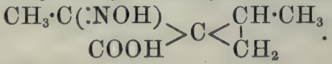
In order to obtain sufficient material for our experiments, the fraction of the ethereal salt boiling at 195—225° (preceding section), and which consists for the most part of ethyl acetylmethyltrimethylenecarboxylate, was hydrolysed by boiling with a considerable excess of alcoholic potash, the product filtered from the potassium carbonate which had separated during the operation (due to the hydrolysis of some ethyl acetoacetate present in the ethereal salt employed), the residue washed with alcohol, the filtrate evaporated with the addition of water till free from alcohol, the solution filtered, cooled well, acidified with dilute sulphuric acid, and extracted 10 times with pure ether. The ethereal solution was dried over calcium chloride, evaporated, and the residual brownish oil, which smelt strongly of acetic acid, purified by conversion into the barium salt. For this purpose, the oil was dissolved in a considerable quantity of water, mixed with barium hydrate solution until strongly alkaline, heated to boiling, and a current of carbonic anhydride passed through the liquid until no further precipitation of barium carbonate took place. The product was filtered, the almost colourless solution evaporated to a fairly small bulk, cooled well, acidified with dilute hydrochloric acid, and extracted 10 times with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited an almost colourless oil, which, after standing over sulphuric acid under reduced pressure for 24 hours, gave the following results on analysis:—

0·1460 gram substance gave 0·0973 gram H_2O and 0·3176 gram CO_2.

	Theory.  $\begin{matrix}CH_3\cdot CO\\COOH\end{matrix}>C<\begin{matrix}CH\cdot CH_3\\\vert\\CH_2\end{matrix}$.	Found.	Previous analysis.
C	59·15 per cent.	59·32 per cent.	58·66 per cent.
H	7·05 „	7·40 „	7·52 „
O	33·80 „	33·28 „	33·82 „

This substance is, therefore, almost pure acetylmethyltrimethylenecarboxylic acid, and as such it was employed in the subsequent experiments. This acid is a moderately thick, almost colourless oil, which, in dilute sodium carbonate solution, decolorises potassium permanganate solution instantly, but if excess of potassium permanganate is added, the solution allowed to stand for one hour, the excess of permanganate destroyed, the alkaline solution acidified and extracted with ether, an oily acid is obtained, which no longer decolorises permanganate. This behaviour indicates that the original acid is a mixture of acetylmethyltrimethylenecarboxylic acid and of dimethyldehydropentonecarboxylic acid (compare Trans., 1891, **59**, 864).

Oxime of Acetylmethyltrimethylenecarboxylic Acid,



$$\begin{matrix}CH_3\cdot C(:NOH)\\COOH\end{matrix}>C<\begin{matrix}CH\cdot CH_3\\\vert\\CH_2\end{matrix}.$$

Acetyltrimethylenecarboxylic acid, when treated with hydroxylamine in alkaline solution, readily yields an oxime (Trans., 1891,

59, 867), thus proving that it contains a carbonyl group, and as it was important to show that this acid and acetylmethyltrimethylenecarboxylic acid were similarly constituted, experiments on the action of hydroxylamine on the latter were instituted.

Acetylmethyltrimethylenecarboxylic acid (1 mol.) was dissolved in a little water, mixed with a moderately strong solution of potassium hydrate (5 mols.), a saturated aqueous solution of hydroxylamine (2 mols.) added, and the whole allowed to stand at ordinary temperatures for 24 hours. The product was acidified with dilute hydrochloric acid, extracted several times with ether, and the ethereal extract, after being dried over calcium chloride and evaporated to a small bulk, was transferred to a small dish and allowed to evaporate at the ordinary temperature. The crystals which separated were freed from oily mother liquor by spreading on a porous plate, dried over sulphuric acid under reduced pressure, and then ground up in an agate mortar with a small quantity of pure benzene. In this way a trace of a dark-coloured impurity was dissolved, and after filtering and washing with a little benzene, a colourless, crystalline residue was obtained, which consisted of the almost pure oxime of acetylmethyltrimethylenecarboxylic acid.

The solution of this substance in warm water, when filtered and allowed to stand, deposits the pure oxime in colourless plates, which, after drying first on a porous plate over sulphuric acid under reduced pressure, and then at 80°, gave the following numbers on analysis :—

0·1229 gram substance gave 0·0818 gram H_2O and 0·2416 gram CO_2.

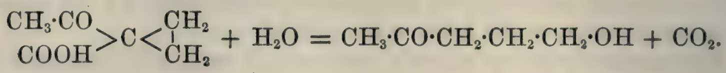
0·1907 gram substance gave 14·6 c.c. N ; $t = 16°$; bar. = 745 mm.

	Theory. $C_7H_{11}NO_3$.	Found.
C	53·50 per cent.	53·61 per cent.
H	7·01 ,,	7·39 ,,
N	8·92 ,,	8·63 ,,

Acetylmethyltrimethylenecarboxylic acid oxime melts at 153—155° with decomposition. It is readily soluble in warm water and alcohol, but only sparingly in benzene, and is almost insoluble in light petroleum. It crystallises from water in beautiful, colourless, glistening plates.

Acetoisobutyl Alcohol, $CH_3·CO·CH_2·CH(CH_3)·CH_2·OH$, *and* *Acetoisobutyl Bromide*, $CH_3·CO·CH_2·CH(CH_3)·CH_2Br$.

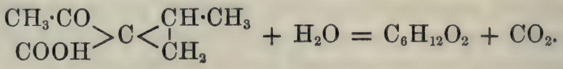
The action of water on acetyltrimethylenecarboxylic acid was first investigated by Freer and Perkin (Trans., 1887, **51**, 829), who showed that, on prolonged boiling with water, it is decomposed into acetopropyl alcohol and carbonic anhydride, thus:—



$$\begin{matrix}CH_3\cdot CO\\ COOH\end{matrix}\!>\!C\!<\!\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} + H_2O = CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH + CO_2.$$

That this was ω-acetyl normal propyl alcohol was subsequently proved by Colman and Perkin (Trans., 1888, **53**, 189) by oxidising the alcohol to levulinic acid.

Similarly, we have found that acetylmethyltrimethylenecarboxylic acid, under analogous conditions, is converted, apparently quantitatively, into an acetobutyl alcohol, thus:—



$$\begin{matrix}CH_3\cdot CO\\ COOH\end{matrix}\!>\!C\!<\!\begin{matrix}CH\cdot CH_3\\ |\\ CH_2\end{matrix} + H_2O = C_6H_{12}O_2 + CO_2.$$

The constitution of the resulting alcohol may be represented by either of the four following formulæ:—

I.	$CH_3\cdot CO\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot OH.$	*Acetoisobutyl alcohol.*
II.	$CH_3\cdot CO\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH_3.$	*Acetopropylcarbinol.*
III.	$CH_3\cdot CO\cdot CH(OH)\cdot CH(CH_3)_2.$	*Acetoisopropylcarbinol.*
IV.	$CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CH_3.$	*Acetoethylmethylcarbinol.*

Acetopropyl alcohol, obtained from acetyltrimethylenecarboxylic acid, is the normal primary alcohol, and as it is extremely probable that the corresponding ketone alcohol obtained from acetylmethyltrimethylenecarboxylic acid is analogously constituted, we shall assume, until evidence to the contrary has been deduced, that this ketone alcohol is acetoisobutyl alcohol,

$$CH_3\cdot CO\cdot CH_2\cdot CH(CH_3)\cdot CH_2\cdot OH.$$

The hydrolysis of acetylmethyltrimethylenecarboxylic acid was carried out by dissolving the acid in 20 times its weight of water, and heating the solution to boiling, in a flask connected with a reflux apparatus, for three days, at the end of which time the evolution of carbonic anhydride had practically ceased. The product was then concentrated by distillation from a flask connected with a long colonna until the greater bulk of the water had been removed, the residue saturated with potassium carbonate, and the turbid liquid, from which, on standing, the alcohol separated as a light, oily layer, extracted 20 times with pure ether. After drying over potassium carbonate and evaporating, a colourless oil was obtained, which, on distillation under reduced pressure, boiled constantly at 140—142° (100 mm.), and gave the following results on analysis:—

0·1478 gram substance gave 0·1393 gram H_2O and 0·3363 gram CO_2.

	Theory. $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}OH$.	Found.
C	62·07 per cent.	62·07 per cent.
H	10·34 ,,	10·49 ,,
O	27·59 ,,	27·44 ,,

Acetoisobutyl alcohol is a colourless liquid, which mixes in all proportions with water, and in its general properties bears a very close resemblance to acetopropyl alcohol and acetobutyl alcohol.

Acetoisobutyl alcohol dissolves in fuming hydrobromic acid with evolution of a considerable amount of heat, and formation of acetoisobutyl bromide, thus:—

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}OH + HBr = CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH_2Br + H_2O.$$

After standing for some time, the product was poured into water, extracted three times with ether, the ethereal solution washed with water, dried over calcium chloride, evaporated, and the residual, yellowish oil distilled under diminished pressure (100 mm.). A considerable quantity of an almost colourless oil was thus obtained boiling at 135—140° (100 mm.), and, on analysis, gave numbers agreeing approximately with those required for acetoisobutyl bromide.

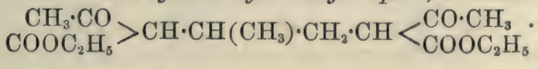
0·1601 gram substance, heated in a sealed tube with nitric acid and silver nitrate at 180° for four hours, gave 0·1625 gram AgBr.

	Theory. $C_6H_{11}BrO$.	Found.
Br	44·69 per cent.	43·18 per cent.

As in the case of acetobutyl bromide and acetopropyl bromide, this substance is evidently partially decomposed on distillation, with loss of hydrogen bromide, and this accounts for the analytical results coming too low.

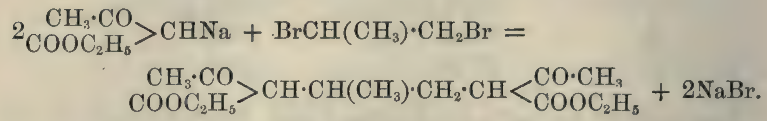
Acetoisobutyl bromide is a thick, colourless oil, which, on standing, rapidly becomes dark coloured; it has a peculiar odour, closely resembling that of acetobutyl bromide or acetopropyl bromide.

Ethyl Methyldiacetyladipate,



$$\begin{matrix}CH_3{\cdot}CO\\COOC_2H_5\end{matrix}{>}CH{\cdot}CH(CH_3){\cdot}CH_2{\cdot}CH{<}\begin{matrix}CO{\cdot}CH_3\\COOC_2H_5\end{matrix}.$$

When ethylene bromide reacts with the sodium compound of ethyl acetoacetate, one of the principal products of the reaction is ethyl diacetyladipate (Trans., 1890, **57**, 205), and when propylene bromide is employed the reaction proceeds, in part, in a precisely similar manner, with formation of ethyl methyldiacetyladipate.



$$2\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}{>}CHNa + BrCH(CH_3)\cdot CH_2Br =$$

$$\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}{>}CH\cdot CH(CH_3)\cdot CH_2\cdot CH{<}\begin{matrix}CO\cdot CH_3\\ COOC_2H_5\end{matrix} + 2NaBr.$$

In order to isolate this substance, the crude product of the action of propylene bromide on the sodium compound of ethyl acetoacetate after extraction with ether, as described on p. 68, was distilled in a current of steam until all the ethyl acetylmethyltrimethylenecarboxylate and unchanged ethyl acetoacetate and propylene bromide had passed over, and until only a very small quantity of oil came over with the condensed steam. The residual, thick, dark-brown oil, which showed properties very similar to those of crude ethyl diacetyladipate (*loc. cit.*, p. 216), was purified by conversion into the sodium compound in the following way:—

The oil, after extracting with ether, drying over calcium chloride, and evaporating, was weighed, dissolved in pure, dry ether, and gradually mixed with an excess of a solution of sodium ethylate, diluted with ether, and allowed to stand for a few minutes. The yellow, flocculent sodium compound, which separated, was collected, washed rapidly with ether, decomposed with dilute sulphuric acid, and the yellowish oil which is thus regenerated extracted with ether. The ethereal solution was then well washed with dilute sodium carbonate solution, dried over calcium chloride, and the conversion into the sodium compound repeated.

In this way a small quantity of a straw-coloured oil was obtained, which, after standing over sulphuric acid under reduced pressure for 24 hours, gave the following results on analysis:—

I. 0·1710 gram substance gave 0·1248 gram H_2O and 0·3802 gram CO_2.

II. 0·1496 gram substance gave 0·1073 gram H_2O and 0·3374 gram CO_2.

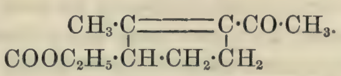
	Theory.	Found.	
	$C_{15}H_{24}O_6$.	I.	II.
C	60·00 per cent.	60·63	61·50 per cent.
H	8·00 ,,	8·11	7·90 ,,
O	32·00 ,,	31·26	30·60 ,,

These numbers agree approximately with those required by the formula $C_{15}H_{24}O_6$.

Ethyl methyldiacetyladipate closely resembles ethyl diacetyladipate in its properties. In alcoholic solution it gives, with a drop of ferric chloride, an intense violet coloration; it combines readily with phenylhydrazine and, apparently, also with ammonia, but owing to the small amount of material at our disposal, these reactions were not further investigated.

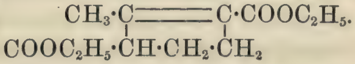
Decomposition of Ethyl Methyldiacetyladipate by Heat.—When subjected to distillation under reduced pressure, ethyl diacetyladipate is decomposed with formation of a variety of substances, of which the most important are the following (Trans., 1890, **57**, 206):—

Ethyl methyldihydropentene-methylketonecarboxylate .



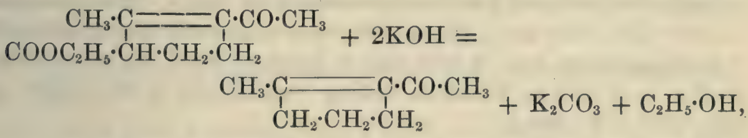
$$\begin{array}{rcl}\mathrm{CH_3\cdot C} & = & \mathrm{C\cdot CO\cdot CH_3.}\\ | & & | \\ \mathrm{COOC_2H_5\cdot CH} & \mathrm{\cdot CH_2\cdot} & \mathrm{CH_2}\end{array}$$

Ethyl methyldihydropentene-dicarboxylate............



$$\begin{array}{rcl}\mathrm{CH_3\cdot C} & = & \mathrm{C\cdot COOC_2H_5.}\\ | & & | \\ \mathrm{COOC_2H_5\cdot CH} & \mathrm{\cdot CH_2\cdot} & \mathrm{CH_2}\end{array}$$

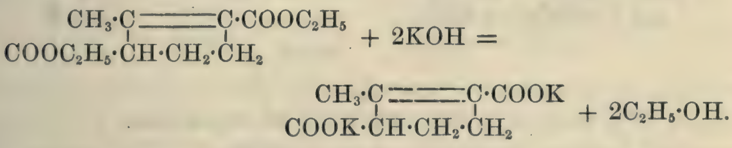
The first of these substances, on hydrolysis, yields methyldihydropentene methyl ketone, thus:—



$$\begin{array}{rcl}\mathrm{CH_3\cdot C} & = & \mathrm{C\cdot CO\cdot CH_3}\\ | & & | \\ \mathrm{COOC_2H_5\cdot CH} & \mathrm{\cdot CH_2\cdot} & \mathrm{CH_2}\end{array} + 2\mathrm{KOH} =$$

$$\begin{array}{rcl}\mathrm{CH_3\cdot C} & \text{———} & \mathrm{C\cdot CO\cdot CH_3}\\ | & & | \\ \mathrm{CH_2} & \mathrm{\cdot CH_2\cdot} & \mathrm{CH_2}\end{array} + \mathrm{K_2CO_3} + \mathrm{C_2H_5\cdot OH},$$

whereas the second, under similar conditions, is simply converted into the potassium salt of methyldihydropentenedicarboxylic acid, with elimination of alcohol, thus:—



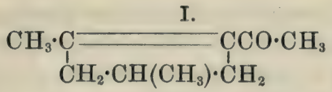
$$\begin{array}{rcl}\mathrm{CH_3\cdot C} & = & \mathrm{C\cdot COOC_2H_5}\\ | & & | \\ \mathrm{COOC_2H_5\cdot CH} & \mathrm{\cdot CH_2\cdot} & \mathrm{CH_2}\end{array} + 2\mathrm{KOH} =$$

$$\begin{array}{rcl}\mathrm{CH_3\cdot C} & = & \mathrm{C\cdot COOK}\\ | & & | \\ \mathrm{COOK\cdot CH} & \mathrm{\cdot CH_2\cdot} & \mathrm{CH_2}\end{array} + 2\mathrm{C_2H_5\cdot OH}.$$

The decomposition of ethyl methyl diacetyladipate on distillation evidently proceeds in an exactly similar manner; but, in this case, owing to the presence of the additional methyl group, it is more difficult to assign the correct constitution to the substances formed.

On hydrolysing the product obtained by the distillation of crude ethyl methyldiacetyladipate, a neutral substance, $C_9H_{14}O$, and an acid, $C_9H_{12}O_4$, are obtained exactly as in the case of ethyl diacetyladipate. The neutral substance, which is obviously *dimethyldihydropentene methyl ketone* may have either of the following formulæ:—

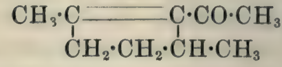
I.



$$\begin{array}{l} CH_3\cdot C = CCO\cdot CH_3 \\ \quad CH_2\cdot CH(CH_3)\cdot CH_2 \end{array}$$

or

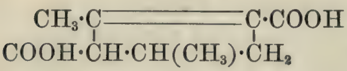
II.



$$\begin{array}{l} CH_3\cdot C = C\cdot CO\cdot CH_3 \\ \quad CH_2\cdot CH_2\cdot CH\cdot CH_3 \end{array},$$

and the constitution of the acid, which is clearly *dimethyldihydropentenedicarboxylic acid*, may be represented thus :—

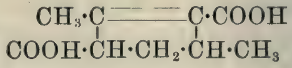
I.



$$\begin{array}{l} \quad CH_3\cdot C = C\cdot COOH \\ COOH\cdot CH\cdot CH(CH_3)\cdot CH_2 \end{array}$$

or

II.



$$\begin{array}{l} \quad CH_3\cdot C = C\cdot COOH \\ COOH\cdot CH\cdot CH_2\cdot CH\cdot CH_3 \end{array}.$$

Unfortunately, with the small amount of material at our disposal, we were not able to decide between these formulæ, but as we consider Formula I in each case to be the more probable, we have, for simplicity's sake, adopted them in this paper.

In carrying out these decomposition experiments, the crude product of the action of propylene bromide on the sodium compound of ethyl acetoacetate was fractioned as described on p. 68 until the thermometer rose to 190°, and the residue, which contains the ethyl methyldiacetyladipate, distilled under reduced pressure (100 mm.). The oil boiling at 130—230° (100 mm.) (C, p. 68), was repeatedly fractioned under reduced pressure, and in this way a straw-coloured oil was obtained in the form of two fractions boiling respectively at 208—211° and 212—215° (175 mm.).

These fractions gave, on analysis, the following numbers :—

I (208—211°). 0·1420 gram substance gave 0·1066 gram H_2O and 0·3432 gram CO_2.

II (212—215°). 0·1528 gram substance gave 0·1120 gram H_2O and 0·3684 gram CO_2.

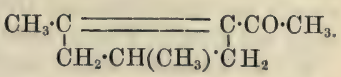
	Found.	
	I.	II.
C	65·91	65·75 per cent.
H...........	8·34	8·14 ,,

The principal product of the distillation of ethyl diacetyladipate boiled constantly at 230—231° (200 mm.), and gave on analysis the following numbers as the mean of four experiments :—

C........	62·93 per cent.
H	7·83 ,,

The difference between these numbers and those obtained above is amply accounted for by the introduction of an extra methyl group, and although the products in both cases are mixtures, there can be no doubt, from the study of their behaviour on hydrolysis, that they are analogously constituted.

Dimethyldihydropentene Methyl Ketone,



$$\begin{array}{l} CH_3\cdot C = C\cdot CO\cdot CH_3. \\ \quad | \qquad\qquad\qquad | \\ CH_2\cdot CH(CH_3)\cdot CH_2 \end{array}$$

This substance is produced in considerable quantity by the hydrolysis of the crude ethereal salt boiling at 200—220° (175 mm.), obtained as explained in the previous section.

20 grams of this oil was digested with a moderately strong solution of 35 grams of potassium hydrate in absolute alcohol, in a flask connected with a reflux apparatus, for three hours on a water-bath. During the operation, a large amount of potassium carbonate separated, and the liquid became brownish, and acquired a strong odour of peppermint. The product was mixed with water, extracted five times with ether, the ethereal solution washed with water, dried over calcium chloride, evaporated, and the residual yellowish oil purified by fractional distillation. The principal fraction obtained was an almost colourless oil boiling at 195—205°, but a considerable residue was left in the retort which will be referred to again later on. The fraction 195—205° was again distilled, and the portion boiling at 198—200° analysed with the following result:—

I. 0·1570 gram substance gave 0·1444 gram H_2O and 0·4481 gram CO_2.

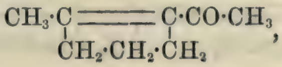
II. 0·1428 gram substance gave 0·1292 gram H_2O and 0·4070 gram CO_2.

	Theory. $C_9H_{14}O$.	Found. I.	II.
C	78·26 per cent.	77·84	77·73 per cent.
H	10·15 ,,	10·21	10·05 ,,
O	11·60 ,,	11·95	12·22 ,,

Dimethyldihydropentene methyl ketone is a colourless oil, smelling strongly of peppermint, which, on standing in the light, rapidly decolorises, and it is remarkable that this oil, on repeated fractionation, sometimes yields a dark-brown distillate.

This behaviour is probably caused by the absorption of oxygen during the distillation, and this may be an explanation of the fact that one or two preparations of this ketone, on analysis, gave results considerably too low in carbon and slightly too low in hydrogen.

Dimethyldihydropentene methyl ketone in its general properties resembles closely the corresponding monomethyl derivative,



$$\begin{array}{l} CH_3\cdot C = C\cdot CO\cdot CH_3, \\ \qquad | \qquad\quad | \\ \quad CH_2\cdot CH_2\cdot CH_2 \end{array}$$

obtained by the hydrolysis of ethyl diacetyladipate with alcoholic potash (Trans., 1890, **57**, 232) and by the action of dehydrating agents on diacetylbutane, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$ (Marshall and Perkin, Trans., 1890, **57**, 242).

It is isomeric with methyltetrahydrobenzene methyl ketone, $CH_2{<}\begin{matrix}CH_2\cdot C(CH_3)\\ CH_2 — CH_2\end{matrix}{>}C\cdot CO\cdot CH_3$, a substance produced by the action of dehydrating agents on diacetylpentane (Kipping and Perkin, Trans., 1890, **57**, 16), and which boils at 205—206°.

The thick, dark-brown oil boiling above 210° which remains in the retort after the above ketone has distilled over was collected from several operations, and distilled under reduced pressure (30 mm.); in this way a quantity of a thick, yellowish oil was obtained boiling at 230—240° (30 mm.). On analysis, it gave the following numbers:—

0·1638 gram substance gave 0·1540 gram H_2O and 0·5070 gram CO_2.

	Theory. $C_{18}H_{26}O$.	Found.
C	83·72 per cent.	84·41 per cent.
H	10·08 ,,	10·44 ,,
O	6·20 ,,	5·15 ,,

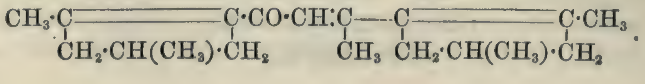
A determination of the molecular weight of this substance by Raoult's method, using acetic acid as the solvent, gave the following results:—

Substance taken................	0·9828 gram.
Acetic acid taken	32·5 grams.
Melting point of the acetic acid ..	16·19°
Melting point of the mixture	15·73°
Depression of the melting point ..	0·46°
Molecular weight, $C_{18}H_{26}O$	258
Found	257

This substance has, therefore, the formula $C_{18}H_{26}O$, and is obviously produced by the condensation of 2 mols. of dimethyldihydropentene methyl ketone with the elimination of 1 mol. of water.

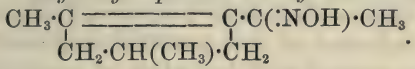
$$2C_9H_{14}O = C_{18}H_{26}O + H_2O.$$

Assuming this condensation to take place in the same way as the condensation of 2 mols. of acetone in forming mesityl oxide, the constitution of the substance $C_{18}H_{26}$ would be represented by the formula



$$\begin{array}{ccccccc} CH_3\cdot C & = & C\cdot CO\cdot CH{:}C & - & C & = & C\cdot CH_3 \\ | & & |\qquad | & & | & & | \\ CH_2\cdot & CH(CH_3) & \cdot CH_2\quad CH_3 & & CH_2\cdot & CH(CH_3) & \cdot CH_2 \end{array}.$$

Dimethyldihydropentene Methyl Ketoxime,



$$\begin{array}{l} CH_3\cdot C = = = = = = C\cdot C(:NOH)\cdot CH_3 \\ \qquad CH_2\cdot CH(CH_3)\cdot CH_2 \end{array}.$$

In order to prepare this oxime, 5 grams of pure dimethyldihydropentene methyl ketone was dissolved in a little methyl alcohol, mixed with a solution of 12 grams of potassium hydrate dissolved in alcohol, a concentrated aqueous solution of hydroxylamine hydrochloride (5 grams) added, and the whole allowed to stand for 24 hours. The product was transferred to a porcelain dish, gently warmed on a water-bath till free from methyl alcohol, mixed with water, and the oil which separated extracted with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a colourless oil which, on fractionation under reduced pressure (100 mm.), distilled almost entirely between 172° and 176° .

A small quantity of the oil boiling at 175° (100 mm.) gave the following results on analysis :—

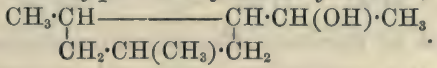
I. 0·1712 gram substance gave 0·1530 gram H_2O and 0·4436 gram CO_2.
0·1571 gram substance gave 13·1 c.c. N ; $t = 20°$; bar. = 740 mm.
II. 0·1739 gram substance gave 0·1592 gram H_2O and 0·4469 gram CO_2.

	Theory.	Found.	
	$C_9H_{15}NO$.	I.	II.
C	70·58 per cent.	70·66	70·08 per cent.
H	9·80 ,,	9·93	10·17 ,,
N	9·15 ,,	9·27	— ,,

Dimethyldihydropentene methyl ketoxime is a thick, pale-yellow oil, possessing the odour characteristic of oximes.

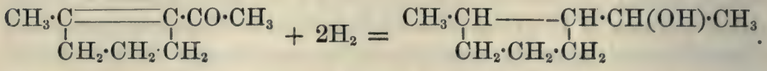
It is only sparingly soluble in cold, dilute, aqueous potassium hydrate, but dissolves readily in a moderately strong solution on warming, forming a colourless solution which, on cooling, deposits a white, crystalline potassium salt. This oxime is isomeric with orthomethyltetrahydrobenzene methyl ketoxime (Kipping and Perkin, Trans., 1890, **57**, 18).

Dimethylpentamethylenemethylcarbinol,



$$\begin{array}{l} CH_3\cdot CH \text{———————} CH\cdot CH(OH)\cdot CH_3 \\ \qquad CH_2\cdot CH(CH_3)\cdot CH_2 \end{array}.$$

In studying the action of reducing agents on methyldihydropentene methyl ketone, Marshall and Perkin (Trans., 1890, **57**, 245 found that this unsaturated ketone, when treated with sodium in moist ethereal solution, is not only converted into the carbinol, but that, under the influence of this powerful reagent, the double band in the ring is also reduced with formation of methylpentamethylenemethylcarbinol, thus:—



$$\begin{array}{l} CH_3\cdot C{=\!=\!=\!=}C\cdot CO\cdot CH_3 \\ \quad CH_2\cdot CH_2\cdot CH_2 \end{array} + 2H_2 = \begin{array}{l} CH_3\cdot CH{-\!-\!-}CH\cdot CH(OH)\cdot CH_3 \\ \quad CH_2\cdot CH_2\cdot CH_2 \end{array}.$$

Similar results were obtained by Kipping and Perkin in studying the action of reducing agents on orthomethyltetrahydrobenzene methyl ketone (Trans., 1890, **57**, 21).

This interesting point led us to experiment on the behaviour of dimethyldihydropentene methyl ketone when treated with sodium in moist ethereal solution; and we find that this ketone, under these conditions, also takes up 4 atoms of hydrogen with formation of dimethylpentamethylenemethylcarbinol.

About 15 grams of the pure ketone was dissolved in ether, the solution floated on a solution of sodium hydrate, and treated carefully with a very large excess of sodium, small quantities of water being added when necessary, and the reaction moderated by cooling the flask containing the mixture by a stream of water. During the operation, a quantity of a white sodium compound often separates, especially if the reduction is slowly conducted. This is obviously the sodium compound of the carbinol; it may be readily decomposed by the addition of water and gently agitating the flask. The ethereal solution was ultimately separated, washed with a little dilute hydrochloric acid, dried over calcium chloride, evaporated, and the residual almost colourless oil purified by repeated fractionation under reduced pressure.

The oil was thus separated into two substances, boiling respectively at 184—187° (100 mm.) and 230—240° (70 mm.).

The former of these gave, on analysis, the following numbers:—

0·1062 gram substance gave 0·1213 gram H_2O and 0·2970 gram CO_2.

	Theory.		
	$C_9H_{18}O$.	$C_9H_{16}O$.	Found.
C	76·07	77·14 per cent.	76·27 per cent.
H	12·67	11·43 ,,	12·69 ,,
O	11·27	11·43 ,,	11·04 ,,

This substance is, therefore, dimethylpentamethylenemethylcarbinol, $C_9H_{18}O$. It is a colourless, mobile oil, possessing an odour resembling that of menthol; when digested with acetic anhydride, it yields an acetate boiling at 200—202°.

The second substance, which is produced in small quantities during the reduction of the ketone, and boils at 230—240° (70 mm.), is a very thick, almost colourless oil; on standing, it showed no signs of crystallising.

It yielded the following numbers on analysis:—

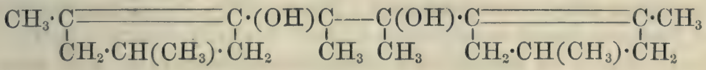
0·1212 gram substance gave 0·1220 gram H_2O and 0·3474 gram CO_2.

	Theory. $C_{18}H_{30}O_2$.	Found.
C	77·69 per cent.	78·17 per cent.
H	10·80 „	11·18 „
O	11·51 „	10·65 „

The molecular weight of this substance was determined by Raoult's method, using acetic acid as the solvent. The following results were obtained:—

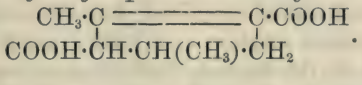
Weight of substance taken................	0·6676 gram
Weight of acetic acid	22·64 grams
Melting point of acetic acid	16·19°
Melting point of mixture....................	15·745°
Depression of the melting point............	0·445°
Molecular weight, $C_{18}H_{30}O_2$.................	278
Found..................................	258

This substance has therefore the formula $C_{18}H_{30}O_2$, and, from its mode of preparation and general properties, it is probably a pinacone of the formula



$$\begin{array}{l} CH_3\cdot C{=\!=\!=\!=\!=\!=}C\cdot(OH)C{-\!-}C(OH)\cdot C{=\!=\!=\!=\!=\!=}C\cdot CH_3 \\ \quad | \qquad\qquad\qquad\quad | \quad\;\; | \qquad\; | \qquad\quad | \qquad\qquad\qquad\quad | \\ \quad CH_2\cdot CH(CH_3)\cdot CH_2 \quad CH_3 \;\; CH_3 \quad CH_2\cdot CH(CH_3)\cdot CH_2 \end{array}$$

Dimethyldihydropentenedicarboxylic Acid,



$$\begin{array}{l} \qquad\quad CH_3\cdot C{=\!=\!=\!=}C\cdot COOH \\ \qquad\qquad\quad | \qquad\qquad\; | \\ COOH\cdot CH\cdot CH(CH_3)\cdot CH_2 \end{array}.$$

The brownish alkaline solution from the hydrolysis of the oil, b. p. 200—205° (175 mm.), obtained by the distillation of ethyl methyldiacetyladipate, from which the crude dimethyldihydropentene methyl ketone had been extracted with ether, as described on p. 77, contains the potassium salt of dimethyldihydropentenedicarboxylic acid.

In order to isolate the acid, the alkaline solution was acidified with hydrochloric acid, extracted five times with ether, the ethereal solution dried over calcium chloride, evaporated, and the dark-brownish, oily residue allowed to stand over sulphuric acid under reduced pressure for several days. As the oil showed no signs of crystallising, it was dissolved in a considerable quantity of water, mixed with barium hydrate solution until distinctly alkaline, heated to boiling, and a current of carbonic anhydride passed until the excess of barium hydrate had been removed. The product was filtered, the filtrate acidified with hydrochloric acid, extracted with ether, the ether evaporated, and the residue, which was much improved in appearance, again treated with barium hydrate as before. The ethereal extract ultimately obtained was dried over calcium chloride, evaporated, and the residual yellow oil allowed to stand over sulphuric acid, under reduced pressure, for some weeks, until it had almost completely solidified.

The crude substance was spread on a porous plate till free from oily impurity, recrystallised twice from water, and the straw-coloured, nodular masses thus obtained, after drying in a desiccator, analysed with the following result:—

0·1808 gram substance gave 0·1083 gram H_2O and 0·3905 gram CO_2.

	Theory. $C_9H_{12}O_4$.	Found.
C......	58·69 per cent.	58·90 per cent.
H......	6·52 ,,	6·65 ,,
O......	34·79 ,,	34·45 ,,

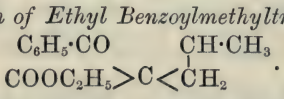
Dimethyldihydropentenedicarboxylic acid melts at 180—182° with slight previous softening, and in its general properties bears a very close resemblance to methyldihydropentenedicarboxylic acid obtained from ethyl diacetyladipate (Trans., 1890, **57**, 233); the former was, however, found much more difficult to purify than the latter.

The basicity of dimethyldihydropentenedicarboxylic acid was determined by titration with standard potassium hydrate solution (1 c.c. = 0·00559 gram KOH).

0·2630 gram substance required for neutralisation 29·2 c.c. of potassium hydrate solution = 0·1632 gram KOH.

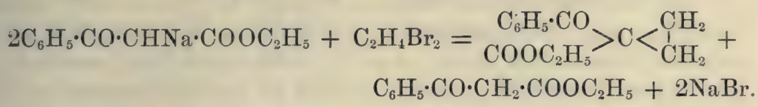
A bibasic acid of the formula $C_9H_{12}O_4$ requires 0·1600 gram KOH for neutralisation.

Action of Propylene Bromide on the Sodium Compound of Ethylbenzoylacetate. Formation of Ethyl Benzoylmethyltrimethylenecarboxylate,



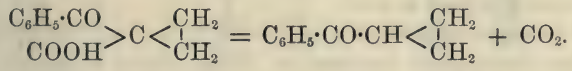
$$\begin{array}{l} C_6H_5\cdot CO \\ COOC_2H_5 \end{array}\!\!>C<\!\!\begin{array}{l} CH\cdot CH_3 \\ \;| \\ CH_2 \end{array}.$$

It has been shown in previous researches (Trans., 1885, **47**, 836; 1887, **51**, 837; 1891, **59**, 833) that the sodium compound of ethyl benzoylacetate, when treated with ethylene bromide at 100° in alcoholic solution, yields ethyl benzoyltrimethylenecarboxylate, thus:—



$$2C_6H_5{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5 + C_2H_4Br_2 = {C_6H_5{\cdot}CO \atop COOC_2H_5}{>}C{<}{CH_2 \atop CH_2} + C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 + 2NaBr.$$

This ethereal salt, on hydrolysis, yields the corresponding benzoyltrimethylenecarboxylic acid, which, when distilled, is converted quantitatively into benzoyltrimethylene with evolution of carbonic anhydride, thus:—



$${C_6H_5{\cdot}CO \atop COOH}{>}C{<}{CH_2 \atop CH_2} = C_6H_5{\cdot}CO{\cdot}CH{<}{CH_2 \atop CH_2} + CO_2.$$

While studying the action of propylene bromide on the sodium compound of ethyl acetoacetate, it occurred to us that it would be interesting to include the sodium compound of ethyl benzoylacetate in our investigations, and, as a result of our experiments, we find that the decomposition in this case takes place exactly as in the case of ethylene bromide, yielding derivatives of benzoylmethyltrimethylene.

78 grams of ethyl benzoylacetate was dissolved in a solution of 9·5 grams of sodium in 100 grams of alcohol, mixed with 80 grams of propylene bromide, and the mixture heated in soda-water bottles at 100° for three hours. The product was diluted with water, extracted four times with ether, the ethereal solution well washed, dried over calcium chloride, and the dark-brown, oily residue (73 grams) fractioned under reduced pressure (100 mm.).

In the first distillation, the following fractions were obtained:—

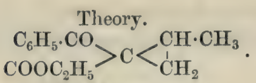
140—160°	about	28	grams.
160—210	,,	11	,,
210—230	,,	25	,,

The fraction 140—160° was found to consist principally of acetophenone; the fractions 160—230° contain, besides a little acetophenone, ethyl benzoylmethyltrimethylenecarboxylate and unchanged ethyl benzoylacetate. From these fractions, on repeated distillation, an oil (9 grams) was ultimately obtained boiling constantly at 223—226° (100 mm.); this, on analysis, gave the following numbers:—

I. 0·2100 gram substance gave 0·1304 gram H_2O and 0·5530 gram CO_2.

II. 0·1575 gram substance gave 0·0970 gram H_2O and 0·4138 gram CO_2.

Theory.



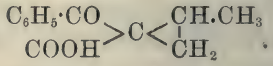
$\begin{matrix}C_6H_5{\cdot}CO\\COOC_2H_5\end{matrix}>C<\begin{matrix}CH{\cdot}CH_3\\|\\CH_2\end{matrix}.$

	Theory.	Found. I.	Found. II.
C	72·41 per cent.	71·92	71·65 per cent.
H	6·89 ,,	6·89	6·84 ,,
O	20·69 ,,	21·19	21·51 ,,

It still contains traces of ethyl benzoylacetate, however, as is shown by the fact that a drop of the oil dissolved in a little alcohol gives a purple coloration with ferric chloride, and it is to the presence of traces of this substance that the slight deficiency in carbon found in the above analyses is due.

Ethyl benzoylmethyltrimethylenecarboxylate is an almost colourless oil which, when pure, appears to distil under ordinary pressures almost without decomposition; in its general properties, it bears a close resemblance to ethyl benzoyltrimethylenecarboxylate.

Benzoylmethyltrimethylenecarboxylic Acid,



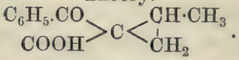
$\begin{matrix}C_6H_5{\cdot}CO\\COOH\end{matrix}>C<\begin{matrix}CH.CH_3\\|\\CH_2\end{matrix}.$

In order to prepare this acid, the pure ethereal salt (1 mol.) was digested with a moderately concentrated solution of potassium hydrate (2 mols.) in methyl alcohol for three hours, the solution diluted with water, evaporated on a water-bath till quite free from methyl alcohol, cooled well, filtered, acidified with dilute hydrochloric acid, and extracted three or four times with pure ether.

The ethereal solution was dried over calcium chloride, evaporated, and the residual yellow oil allowed to stand for some days. The crystals which formed were separated from the oily mother liquor by spreading on a porous plate, and the almost colourless residue washed as rapidly as possible with small quantities of ether on a filter pump. The beautiful, colourless, glistening, crystalline mass thus obtained, after drying over sulphuric acid under reduced pressure, gave the following results on analysis:—

0·1825 gram substance gave 0·1246 gram H_2O and 0·5503 gram CO_2.

Theory.

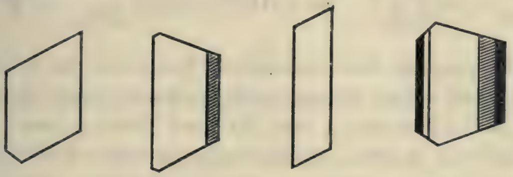


$\begin{matrix}C_6H_5.CO\\COOH\end{matrix}>C<\begin{matrix}CH{\cdot}CH_3\\|\\CH_2\end{matrix}.$

	Theory.	Found.
C	70·59 per cent.	70·66 per cent.
H.......	5·88 ,,	6·04 ,,
O	23·53 ,,	23·30 ,,

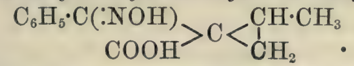
Benzoylmethyltrimethylenecarboxylic acid melts at 128—129°, and at 140° it begins to decompose with evolution of carbonic anhydride.

It is readily soluble in alcohol and benzene, moderately soluble in ether and hot water, sparingly soluble in light petroleum and cold water. The solution of the acid in dilute sodium carbonate does not decolorise potassium permanganate even on long standing. The acid crystallises from its solution in warm water in curiously striated needles grouped together in stellate masses. On examination under the microscope, some of the more perfect crystals were found to have the following forms:—



The acid crystallises from a mixture of benzene and light petroleum in hard, colourless prisms, the surfaces of which are usually very striated and the edges uneven.

Oxime of Benzoylmethyltrimethylenecarboxylic Acid,



$$\begin{matrix}C_6H_5\cdot C(\colon NOH)\\ COOH\end{matrix}>C<\begin{matrix}CH\cdot CH_3\\ |\\ CH_2\end{matrix}\cdot$$

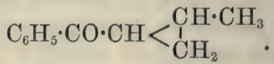
This substance is readily obtained by dissolving pure benzoylmethyltrimethylenecarboxylic acid in a large excess of aqueous potassium hydrate solution, adding twice the calculated quantity of hydroxylamine hydrochloride, and allowing the mixture to stand for two days. The product was warmed for a few minutes at 40—50°, cooled again, acidified with dilute hydrochloric acid, and the oxime, which separates at once in a solid condition, collected, washed with water, and spread on a porous plate. An analysis of the substance, dried over sulphuric acid under reduced pressure, gave the following numbers:—

0·1320 gram substance gave 7·6 c.c. N; $t = 16°$; bar. = 756 mm.

	Theory. $C_{12}H_{13}NO_3$.	Found.
N.......	6·39 per cent.	6·67 per cent.

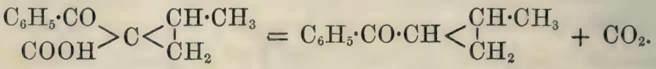
The oxime prepared in this way melts at about 130—135° with decomposition. It is more readily soluble in hot water than the acid itself, but does not crystallise out well on cooling; it dissolves easily in ether and alcohol, but only sparingly in benzene and light petroleum. Unfortunately, owing to the very small amount of material at our disposal, we were not able to recrystallise this oxime, so that the melting point given above must be taken as approximate only.

Benzoylmethyltrimethylene,



$$C_6H_5\cdot CO\cdot CH<\begin{array}{l}CH\cdot CH_3\\ CH_2\end{array}.$$

When heated above 140°, benzoylmethyltrimethylenecarboxylic acid is gradually decomposed with evolution of carbonic anhydride and formation of benzoylmethyltrimethylene, thus :—



$$\begin{array}{r}C_6H_5\cdot CO\\ COOH\end{array}>C<\begin{array}{l}CH\cdot CH_3\\ CH_2\end{array} = C_6H_5\cdot CO\cdot CH<\begin{array}{l}CH\cdot CH_3\\ CH_2\end{array} + CO_2.$$

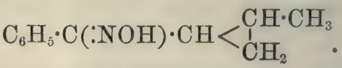
In order to prepare this substance, the crude acid, prepared by hydrolysing crude ethyl benzoylmethyltrimethylenecarboxylate boiling at 210—235° (100 mm.), was distilled from a small retort, the distillate dissolved in ether, shaken once or twice with dilute sodium carbonate solution in order to remove benzoic acid, dried over calcium chloride, evaporated, and the residual almost colourless oil purified by fractionation under ordinary pressures. In this way a small quantity of a straw-coloured oil was obtained boiling at 240—245°, which, on analysis, gave the following numbers :—

0·1825 gram substance gave 0·1246 gram H_2O and 0·5503 gram CO_2.

	Theory. $C_{11}H_{12}O$.	Found.
C	82·50 per cent.	82·23 per cent.
H	7·50 ,,	7·64 ,,
O	10·00 ,,	10·13 ,,

Benzoylmethyltrimethylene is an almost colourless oil slightly soluble in boiling water; it boils at 240—245°, and in its general properties closely resembles benzoyltrimethylene, which boils at 239° (720 mm.).

Benzoyltrimethylene Oxime,



$$C_6H_5\cdot C(:NOH)\cdot CH<\begin{array}{l}CH\cdot CH_3\\ CH_2\end{array}.$$

In order to prepare this oxime, pure benzoylmethyltrimethylene was dissolved in methyl alcohol, mixed with a concentrated aqueous solution of 1½ times the calculated quantity of hydroxylamine hydrochloride, and then four times the calculated quantity of a moderately strong solution of potassium hydrate in methyl alcohol slowly added.

After standing for 24 hours, the product was gently heated on a water-bath till free from alcohol, diluted with water, and extracted three times with pure ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited an almost colourless oil, which, even on long standing over sulphuric acid under reduced pressure, showed no signs of crystallising.

An analysis of this oxime gave the following numbers :—

0·2272 gram substance gave 15·7 c.c. N ; $t = 17°$; bar. = 750 mm.

	Theory. $C_{11}H_{13}NO$.	Found.
N	8·00 per cent.	8·00 per cent.

V.—*The Iodometric Estimation of Chloric Acid in Chlorates.*

By GEORGE MCGOWAN, Ph.D.

IN the memorable paper by Bunsen,* in which he describes the volumetric method for the determination of free iodine, by means of a dilute aqueous solution of sulphurous acid,† and thereby of those substances which yield chlorine quantitatively when warmed with hydrochloric acid ; chlorates are adduced by him as being among the many compounds to which the method is applicable. On pp. 282—3 of Bunsen's paper (*loc. cit.*), one example of the analysis of a chlorate is given, the actual result of which agrees well with theory (that is, that 1 mol. of chloric acid is equivalent to 6 atoms of chlorine or iodine). Finkener,‡ however, afterwards stated that by this process less than the theoretical amount of free chlorine was invariably obtained ; and he recommended, in consequence, a modification of the method, the details of which are to be found either in H. Rose's *Handbuch*, or in the last edition of Fresenius' *Quantitative Analysis*.§

In the *Zeitschrift für angewandte Chemie* for August, 1890 (pp. 477—481), De Koninck and Nihoul published a paper on the iodometric estimation of nitrates and chlorates, their process consisting in the decomposition of a rather concentrated solution of a nitrate or chlorate by gaseous hydrogen chloride in an atmosphere of carbon dioxide, and by this means they obtained excellent results in both cases. The author, independently of the two gentlemen just named, shortly afterwards hit upon the same idea for the estimation of nitrates,* but the details of the method and the apparatus employed differed materially in the two cases, as will be seen by reference to the original papers. He has since then carefully investigated the method as applied to chlorates, and it will be seen that the results, appended below, corroborate those of De Koninck and Nihoul, thus proving that Finkener was mistaken in supposing that the amount of chlorine actually found is less than that required by theory. This error on Finkener's part doubtless arose from a small portion of the chlorine in his experiments being lost by acting on the rubber tubing of his apparatus.

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* "Ueber eine volumetrische Methode von sehr allgemeiner Anwendbarkeit," *Annalen*, **86**, 264—291 (1853).

† This method was originally discovered by Dupasquier, but subsequently improved and elaborated by Bunsen, the solution of sulphurous acid being ultimately replaced by one of sodic thiosulphate.

‡ H. Rose's *Handbuch der anal. Chemie*, 6th Edition, completed by Finkener.

§ 6th German Edition, **1**, 533.

The details of the experiments, about to be cited, are as follows:—

The burettes used were carefully calibrated, and were kept clean by frequent washing with a solution of alcoholic potash.

The thiosulphate solutions employed were standardised with the utmost care from a nearly deci-normal solution of potassic dichromate. This dichromate was recrystallised from the commercial salt, in small crystals, three times, drained (*not* pressed between paper), and dried at 100°; the portion used for making the standard solution was previously heated just to fusion, and cooled over chloride of calcium. The standardising of the thiosulphate was carried out as recommended by Mohr,† that is, a given volume (20—to 30 c.c.) of the dichromate solution was run into a flask provided with a well-fitting glass stopper, a solution of iodide of potassium and concentrated hydrochloric acid were then added in excess, the stopper firmly inserted, and the flask warmed gently in hot water (to about 40°) for a few minutes; it was then quickly cooled, and its contents titrated with the thiosulphate solution.

The potassium chlorate used for the test analyses was recrystallised twice from the commercial salt, in small crystals, drained, dried in the air-bath, finely powdered, and then dried again at 170—200°.

The apparatus employed was that drawn and described in the Transactions, 1891, **59**, 531, except that it was improved by substituting a tight ground-glass joint for the small rubber joint at *o* (see note on p. 532); and, since it is unnecessary in this estimation to previously expel the air present by a current of carbon dioxide, those tubes which come after the tower E were dispensed with. The details of the operation are also practically the same as in the case of a nitrate, only simpler. Comparatively dilute hydrochloric acid may be employed (how dilute it may be, I have not thought it necessary to determine), and the carbon dioxide is required merely to ensure a regular passage of the vapours through the iodide of potash solution, and to prevent any chlorine escaping backwards. This is tested, as before, by the small piece of iodide of starch paper in tube *s*, which should be so placed as never to get warm.

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* "The Iodometric Estimation of Nitric Acid in Nitrates," Trans., 1891, **59**, 530.

† Sutton's *Volumetric Analysis*, 4th Edition, p. 100.

The chlorate is weighed out into the dry evolution flask A, then dissolved in 8 to 10 c.c. of water, and, after all the necessary connections have been made, 8 to 10 c.c. of pure concentrated hydrochloric acid are run in through the funnel *g*. Since the reaction begins in the cold, the carbon dioxide must be turned on immediately, and kept passing at the rate of about four bubbles per second. Care should be taken to heat very gently at first, until the bulk of the chlorine has come over, after which the lamp flame may be gradually turned up and the liquid boiled, exactly as in the case of the nitrate; this ensures that no chlorine escapes backwards. And, as before, after all the chlorine has been apparently driven out, and the solution has become colourless, a second quantity of warm hydrochloric acid (1 in 2) is run in, and the boiling repeated for a few minutes.

The following results of five out of six consecutive estimations may be cited (the fifth estimation was accidentally spoilt):—

	Potassium chlorate taken.	Found.	
I ...	0·1873 gram.	0·1870 gram	= 99·81 per cent.
II ...	0·1949 ,,	0·1950 ,,	= 100·05 ,,
III ...	0·2131 ,,	0·2125 ,,	= 99·72 ,,
IV ...	0·10555 ,,	0·1050 ,,	= 99·53 ,,
V ...	0·05625 ,,	0·05596 ,,	= 99·48 ,,

Notes.—It is necessary to work with small quantities, as above, seeing that such a large amount of chlorine, relatively to the chlorate, is set free. For the titration of the liberated iodine in the estimations I, II, and III, a fifth-normal solution (approximately) of thiosulphate was used, that is, 1 c.c. of it was equivalent to 0·0041786 gram $KClO_3$; for estimation IV, also a fifth-normal solution, of which 1 c.c. was equivalent to 0·0041835 gram $KClO_3$; and for estimation V, a deci-normal solution (approximately), of which 1 c.c. was equivalent to 0·0020057 gram $KClO_3$. In IV and V, the small amounts of chlorate employed were not directly weighed, but their equivalents in measured quantities of a solution containing 1·037 grams in 100 c.c. were taken.

There can thus be no doubt as to the exactness of the process. In conclusion, the author would wish again to emphasise the point that all determinations, in which free chlorine is evolved, should be made in some such apparatus as that described above, in which no india-rubber is exposed to the action of the gas.

University College of N. Wales,
Bangor.

VI.—CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Existence of Hyoscyamine in Lettuce.

By T. S. Dymond, F.I.C., Assistant Lecturer in Chemistry to, and Demonstrator in the Research Laboratory of, the Pharmaceutical Society.

Lettuce has been used in medicine from early times, chiefly as a sedative, and at the present day an extract of the plant is somewhat largely employed. This is prepared by pressing out the juice from the entire fresh plant when in flower, and, after coagulating the proteïd, evaporating the liquid to dryness at a temperature of 60°. My attention was drawn, a few months ago, to the mydriatic action of such an extract, prepared at Hitchin from common lettuce, *Lactuca sativa*. In appearance, odour, and taste it closely resembled the extract of belladonna of the British Pharmacopœia, and, as in belladonna, the mydriatic action was found to be due to an alkaloïd. Nevertheless, the exact history of the extract was known, and 5 grains were swallowed with no more effect than a slight feeling of drowsiness, whilst the same quantity of extract of belladonna would have been a most dangerous dose. It is extraordinary that the similarity in appearance of the extracts of belladonna and lettuce should not have led to the observation that the extract of lettuce exerts a mydriatic action. It seemed possible, however, that contamination of this specimen with a small quantity of extract of belladonna might have occurred, and therefore four other commercial specimens were examined. Three of these had been prepared at Market Deeping, the first from common lettuce, *L. sativa*, the second from wild lettuce, *L. virosa*, the third from that variety of common lettuce especially valued for salad, the cos lettuce. The fourth commercial specimen had been made from wild lettuce, but its exact history was unknown. All the extracts had been prepared from the flowering plant and according to the directions of the British Pharmacopœia.

They all contained a mydriatic alkaloïd in distinct quantity, that from the cos lettuce containing by far the least. Finally, a dried specimen of wild lettuce collected when in flower, when extracted by alcohol acidified by acetic acid, yielded an alkaloïd which dilated the pupil of the eye; a fresh young plant of garden lettuce also yielded a trace of mydriatic substance.

Having now established the fact that both the wild and cultivated lettuce contain at the flowering period a mydriatic alkaloïd, its extraction in a pure state and identification were attempted. Several methods were adopted for separating the alkaloïd from the chlorophyll, fat, sugar, the crystalline substance contained in the milk sap, and the other constituents of the extract.

1. The extract was mixed with water, and the mixture shaken with benzene to remove fat and chlorophyll. The liquid was now made alkaline with sodium carbonate, and the alkaloid removed by shaking with chloroform. The method was a very tedious one, owing to the difficulty of separating the benzene and chloroform from the aqueous liquids.

2. The extract was mixed with dilute hydrochloric acid, and the mixture filtered. To the brown filtrate from the residue of chlorophyll and albuminous matter, alcohol was added. The brown precipitate was filtered off, and the nearly colourless alcoholic filtrate evaporated to a small bulk. The alkaloïd was extracted from the remaining liquid, after rendering it alkaline by sodium carbonate, by agitation with chloroform. This was also a tedious method, owing to the difficulty of filtering the acid liquid from the chlorophyll and proteïd.

3. The extract was dried and roughly powdered. The dry powder being very hygroscopic, it was mixed with an equal volume of sand to prevent the formation of a solid cake and to form a porous mass. This was alternately macerated and percolated with absolute alcohol until the soluble constituents had been almost entirely removed. The alcohol was distilled off, and a residue was obtained containing, besides the alkaloïd, chlorophyll, fat, sugar, and other substances. Water was added, the mixture filtered, the filtrate well shaken with ether, then rendered alkaline with ammonia, and the alkaloïd removed by chloroform. This method is also very tedious. The maceration and percolation of the dried extract by alcohol had to be repeated more than 20 times.

4. The extract was mixed with water acidified with acetic acid, and, to the thick liquid, alcohol was added till the insoluble substances were completely precipitated. The mixture was then filtered, the pale-green filtrate evaporated to a small bulk, filtered again, washed by shaking with ether, and finally rendered alkaline with ammonia, and the alkaloïd removed by shaking with chloroform. This process may be very quickly performed, and yields the alkaloïd in quite as pure a state as the other methods do.

The alkaloïd must in each case be purified by extracting from the solution in chloroform with dilute sulphuric acid, and, after rendering the acid solution alkaline with ammonia, shaking out the alkaloïd with ether. On evaporating the ether, a light-brown, syrupy, alkaloïdal residue is obtained, having powerful mydriatic properties and when the extract of cultivated lettuces had been used a strong odour resembling that of pyridine. (The alkaloïd obtained from the extract of wild lettuce was devoid of this odour.) The pyridine-like body volatilises on exposure to the air, but an impurity remains associated with the alkaloïd which is much more difficult to remove. Purification may be partially effected by taking advantage of the greater solubility of the alkaloïd in ether, and of the fact that, on fractionally precipitating it from an acid solution by ammonia, the impurity is precipitated first, but the complete purification of the alkaloïd was not possible by either method. The presence of the impurity made it impossible to obtain a crystalline aurochloride, although many attempts were made to do so; indeed, these failures at one time suggested that the alkaloïd might prove to be a new member of the mydriatic group (atropine, hyoscyamine, hyoscine, &c.), since all the known members form crystalline aurochlorides.

In attempting to devise a new method of purification, it became necessary to examine the properties of some of the salts of atropine and hyoscyamine. It was found that they both form crystalline oxalates, soluble in alcohol and precipitated from the alcoholic solution by ether. This property was made use of for purifying the lettuce alkaloïd; to its alcoholic solution, an alcoholic solution of oxalic acid was added and the oxalate formed precipitated by ether. The excess of oxalic acid, together with the impurity, remain in solution. The oxalate is redissolved in alcohol and reprecipitated by ether, and is then dissolved in water, the aqueous solution made alkaline with ammonia, and extracted with ether. The ether, on evaporation, leaves a colourless, syrupy residue, which dissolves in chloroform and reappears in long, silky needles on spontaneous evaporation of the solvent.

The crystalline alkaloïd thus obtained resembled hyoscyamine in appearance and properties, but its melting point, 104·1° (corr.), was somewhat lower than that of pure hyoscyamine, 108·5° (Ladenburg).

In order to further purify and characterise the compound, the aurochloride was prepared. The first few drops of the aqueous solution of gold chloride precipitated a resinous mass when added to the solution of the alkaloïd in dilute hydrochloric acid, but a further addition formed a yellow, pulverulent precipitate, which did not aggregate. The whole precipitate was dissolved in hot water acidified with 0·5 per cent. of hydrochloric acid, the small, insoluble residue being filtered off. A process of fractional crystallisation was now performed, and by this means the greater part of the gold salt was finally obtained in the form of flat, shining needles, melting at 159·75° (corr.) after drying at 100°. This melting point corresponds with that of the aurochloride of hyoscyamine, which, according to Ladenburg, is 159° (*Ber.*, **13**, 109).

From the mother liquors from the hyoscyamine aurochloride, a substance was slowly deposited in small, compact, button-like, crystalline masses. It melted at 149·5°. On recrystallising, it was deposited in the flat needles or leaflets characteristic of the hyoscyamine salt, and, after repeating the recrystallisation, melted at 158·5° (corr.). The peculiar form in which the substance first crystallised was probably due to the presence in the mother liquor of a trace of atropine, which probably had been formed from the hyoscyamine during its isolation and purification.

The gold salt melting at 159·75° was analysed. It was dissolved in dilute hydrochloric acid, and the gold precipitated as sulphide by sulphuretted hydrogen; this was ignited and weighed as metallic gold, and in a second experiment washed free from sulphur by bisulphide of carbon and weighed as sulphide. The filtrate from the gold sulphide was freed from sulphuretted hydrogen by a current of air, rendered alkaline by ammonia, and extracted by chloroform. The alkaloïd obtained by evaporating the chloroform was dried at 100° and weighed.

I. 0·0207 gram substance gave 0·0612 gram gold and 0·0096 gram alkaloïd.

II. 0·0063 gram substance gave 0·0023 gram gold sulphide.

	Found.		Calculated for
	I.	II.	$C_{17}H_{23}NO_3,HAuCl_4$.
Gold......	31·0	31·4 per cent.	31·3 per cent.
Alkaloïd ..	46·3	— ,,	45·9 ,,

The alkaloïd is thus proved to be hyoscyamine. In the small quantity of total alkaloïd at my disposal, no other mydriatic base could be detected beyond the trace of atropine already referred to, and which probably did not exist in the plant. The amount of hyoscyamine contained in the extract of common lettuce does not exceed 0·02 per cent., whilst the fresh plant cannot contain more than 0·001 per cent.

It has thus been shown that at the flowering period lettuce contains hyoscyamine, and it is probably to the presence of this alkaloïd that the sedative and anodyne action of the preparations of the plant is due. That this important constituent has been until now overlooked, although the mydriatic properties of wild lettuce have long been known (*Med. Chir. Review*, 1876, 233), is perhaps due to the belief that the activity of lettuce resided in the dried milk sap, which has been employed in medicine for many years under the name of "lactucarium." The medical evidence on the value of this drug is, however, very conflicting, and Garrod has found (*Med. Times and Gazette*, March 26, 1864) that as a soporific it is quite inert. I have examined specimens of lactucarium of both English and German manufacture, and found that they were entirely free from mydriatic properties; neither did they contain any alkaloïd whatever. The repute in which lactucarium has been held as a soporific is perhaps partly due to its smell, which is suggestive of opium.

In connection with the use of lettuce as a vegetable, the fact that it contains a poisonous alkaloïd is of no great importance. It is only eaten in the earlier stages of its growth, before the bitter taste noticed in the older plant has developed, and while the amount of alkaloïd, if any, is extremely small. Nevertheless, there are instances in which the immoderate consumption of lettuce has led to serious and even fatal results.

It is worthy of remark that lettuce belongs to the natural order *Compositæ*, and it appears this is the first occasion on which hyoscyamine, or any alkaloïd belonging to that mydriatic group, has been found in a plant not belonging to the natural order *Solanaceæ*.

My thanks are due to Professor Dunstan for his advice and help during the course of this investigation, to Messrs. W. Ransom and Son, who first drew my attention to this subject, and to Messrs. Wright, Layman, and Umney for furnishing specimens and information.

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VII.—*Action of Sulphuric Acid on the Bromides of Potassium, Sodium, and Hydrogen.*

By Frank T. Addyman, B.Sc., Queenwood College, Hampshire.

On page 1320 of the Abstracts, 1891, is an abstract from a paper on the "Preparation of Hydrobromic Acid," by Feit and Kubierschky. Seeing that the method there given is nearly identical with the one which has been used by me, from time to time, during the last three years, I decided to publish at once the results obtained so far in this research.

The object in view has been to determine to what extent hydrogen bromide is oxidised by sulphuric acid under varying conditions of mass and dilution. The experiments may, for the sake of convenience, be divided into two sets :—

I. Where concentrated sulphuric acid, in varying quantities, is allowed to act on potassium bromide.

II. Where the sulphuric acid used is dilute.

The difference between these two cases is at once apparent when it is considered that in the second case all the products of the reaction remain in solution, thus finding a position of equilibrium between the two reactions :—

$$2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2,$$

and

$$SO_2 + 2H_2O + Br_2 = H_2SO_4 + 2HBr.$$

In the first case, on the other hand, the gaseous substances are partially or wholly removed; so that the sulphuric acid acts much more completely.

These two sets of experiments are in no way comparable.

Action of Concentrated Sulphuric Acid on Potassium Bromide.

In order to determine the quantitative result of this reaction, several descriptions of apparatus were used, which either collected the bromine evolved, in tubes of amorphous phosphorus and water, or else collected all the products in bulbs containing strong potash. In the first case, the amount of phosphoric acid formed was determined by means of magnesia mixture; in the second, the sulphurous anhydride was oxidised by bromine and estimated as barium sulphate. The first of these methods gave such unsatisfactory results that it was soon discarded, and the results here given were always obtained by the barium sulphate method.

The apparatus at first used for working this method consisted of a flask with a reflux condenser attached, through which the gases might pass into U-tubes containing broken glass and bromine-water. The reason for using a condenser was to prevent any sulphuric acid from distilling over. But this was soon discarded as unnecessary; because, in the first place, it was found that the reaction takes place without any evolution of heat; and, secondly, because the last traces of bromine evolved were easily driven off by heating gently. In no case was the temperature raised above 110°.

The set of experiments of which the results are now published was therefore performed, for the most part, in a flask with a very long neck, the body being of about 200 c.c. capacity, and the neck about 16 inches in length. About 3 inches from the body of the flask a side tube was inserted, which was bent up and down into the shape of a W to prevent any sulphuric acid from being carried over mechanically. This was connected with a Will and Varrentrapp bulb tube, containing strong caustic potash solution, to collect all the gaseous products of the reaction.

The potassic bromide was weighed out and placed in the dry flask, then the concentrated sulphuric acid, sp. gr. 1·84, was poured, from a beaker in which it had been weighed, down the long neck, the beaker with the adhering acid being immediately and rapidly reweighed. A stopper was inserted into the top of the neck of the flask and the reaction allowed to proceed until effervescence stopped. On gently warming, the fumes came off more rapidly but got lighter in colour until at last they became colourless: a slow current of air was then aspirated through the apparatus. This experiment in all cases where 11·9 grams of potassic bromide were used occupied about 35 minutes. The potash was removed to a beaker, and bromine added in excess, then barium chloride was added and the barium sulphate weighed.

It has been found most convenient, for comparison's sake, to act upon the supposition that the whole of the bromine is first liberated as hydrogen bromide and that some of this is then decomposed. Reasons for believing this to be true will be given hereafter. The results of the experiments are, therefore, expressed in terms of the percentage of hydrogen bromide which has been decomposed.

No. of expt.	Weight of H_2SO_4 used.	Weight of KBr used.	Approximate molecular ratio of H_2SO_4 to KBr.	Weight of $BaSO_4$.	Per cent. of HBr decomposed.
1*	10·0510	11·9000	1 : 1	0·9864	8·55
2*	5·2460	11·9000	1 : 2	0·3746	3·22
3	9·7510	11·9034	1 : 1	0·8500	7·30
4	9·6050	11·9062	1 : 1	0·9682	8·31
5	14·8080	11·8996	3 : 2	1·8236	15·53
6	19·5230	11·9000	2 : 1	2·3168	19·88
7	24·6140	11·9000	5 : 2	3·1346	26·91
8	28·9360	11·9070	3 : 1	3·6408	31·30

If this were represented in the form of a curve with the percentage of HBr decomposed for the abscissæ and the number of molecules of H_2SO_4 to one of KBr for ordinates, we should get very nearly a straight line, or, in other words, the amount of decomposition is very nearly proportional to the amount of sulphuric acid used.

The materials in Experiment No. 8 were as large in amount as the apparatus would hold, and as experiments with larger quantities gave results varying with the shape of the vessel employed, it was thought that when so large an excess of sulphuric acid was present that the water formed in the reaction caused no sensible dilution, the hydrogen bromide at first formed was decomposed in quantities varying with the amount of sulphuric acid with which it came in contact. Thus a higher percentage would be decomposed in a deep than in a shallow vessel. To test this, the following experiment was devised :—

---

* Condenser used.

1·4035 grams of potassium bromide was passed up into a graduated tube standing over mercury and 10·6 grams of sulphuric acid was passed up after it by means of a graduated syringe having a long curved end. The bromine formed was absorbed by the mercury to form mercurous bromide, which was not acted upon by the sulphuric acid. This was allowed to stand for a week, shaking every day, and then the gas was transferred to a tube having a stopcock above and thence bubbled through silver nitrate slightly acidified with nitric acid. Only the faintest trace of a precipitate was given, showing that the hydrogen bromide had been entirely decomposed.

This experiment was performed in a graduated tube with the intention of measuring the gases, but the absorption of sulphurous anhydride by sulphuric acid is so great that this was found to be useless; it was therefore repeated several times in a plain tube with a stopcock. In one case it gave no trace whatever of hydrogen bromide, in two others very small traces.

Action of Dilute Sulphuric Acid on the Bromides of Hydrogen, Sodium, and Potassium. Preparation of Pure Hydrobromic Acid.

Method 1.—Barium carbonate was dissolved in crude hydrobromic acid, the solution evaporated to dryness, and the barium bromide extracted with hot alcohol, from which, after filtering, it was allowed to crystallise out. From these crystals of pure barium bromide, pure bromine was obtained. This was effected by distilling it with manganese peroxide and strong sulphuric acid, in a retort which had been fused on to a condenser so as to avoid india-rubber joints.

This pure bromine, after washing and redistillation, was converted into hydrobromic acid by means of amorphous phosphorus and water in the ordinary way.

Method 2.—A saturated solution of barium bromide in water was prepared as in the last method, and 60 per cent. sulphuric acid (sp. gr. = 1·50) added in quantity not quite sufficient to precipitate all the barium. The precipitate of barium sulphate was allowed to subside, the liquid decanted off, and then distilled. The first portion of the distillate was rejected as containing scarcely any acid. The distillation is conducted with a thermometer in the vapour; at first very dilute acid comes over. When, the thermometer being a little over 100°, the temperature begins to rise, as it does rather rapidly after a time, the distillate may be collected. At 122°, acid comes over containing 47 per cent. HBr.

Method 3.—This is very similar to that of Feit and Kubierschky, mentioned at the beginning of this paper. Potassium bromide (which has been heated with bromine to remove iodine, and recrystallised) is dissolved in the requisite quantity of 30 per cent. sulphuric acid (sp. gr. = 1·22) calculated according to the equation

$$H_2SO_4 + KBr = KHSO_4 + HBr.$$

To effect this, it was necessary to heat nearly to boiling. On allowing the solution to cool in an open dish, potassium hydrogen sulphate crystallised out, together with a certain amount of unaltered potassium bromide, which is much less soluble in hydrobromic acid than in water. The liquid was poured off into a retort, and distilled to about one-third of its bulk, when it began to turn yellow. This yellow liquid was next mixed with half its bulk of water, and returned whilst warm to the dish containing the crystals, and, after cooling, was again poured off and distilled until the distillate began to be yellow.

The acid thus prepared always contained traces of sulphuric acid, partly carried over mechanically, and partly formed by the passing over together of bromine and sulphurous anhydride. This sulphuric acid was precipitated by pure barium bromide, and the liquid redistilled. When strong acid was required, the portion boiling at 122° was collected; this contained about 47 per cent. HBr.

It will be found, on referring to Experiments 12, 49, 77, and 89, that 30 per cent. sulphuric acid has no action upon hydrogen bromide, whereas 40 per cent. acid, as used by Feit and Kubierschky, has some slight action (Experiments 16, 54, 80, 81, 93, 94). This was my reason for using the more dilute acid. But as, in all cases, redistillation was necessary, the 40 per cent. sulphuric acid would be just as good.

Method of Experiment.—A solution of hydrogen bromide, or of potassium or sodium bromide, was made up to a certain strength, varying in different experiments. 5 c.c. of this was measured out into a tube, concentrated sulphuric acid added in varying quantities from a tap-burette, and sometimes also water, and the whole mass gradually mixed with a glass stirrer. An exactly similar tube was then filled up to the same level with water, and freshly prepared dilute bromine-water (free from iodine or chlorine) added, until the intensity of colour in the two tubes was the same. Potassium iodide was then added in excess to this aqueous solution, and centi-normal sodic thiosulphate run in until the colour disappeared; the end of the reaction being shown more clearly by adding a little starch-paste when the solution was nearly colourless. In this way the amount of bromine formed was determined. In these experiments, the highest results were obtained when the mixture had stood for about 12 hours, after which it slowly decreased, either from the absorption of water or from the evaporation of bromine.

Experiments with Hydrogen Bromide Solution.

5 c.c. HBr solution contains 0·81 gram HBr.

No. of experiment.	Volume of HBr solution.	Volume of H_2SO_4, 98 per cent.	$\frac{N}{100}$ $Na_2S_2O_3$ required.	Br liberated.	Per cent. of HBr decomposed.	Per cent. of H_2SO_4 in solution (calculated).
	c.c.	c.c.				
9	5	0·3	—	—	—	—
10	,,	0·5	—	—	—	—
11	,,	0·7	—	—	—	20·79
12	,,	1·0	—	trace	—	27·27
13	,,	1·2	0·2	0·00016	0·04	31·03
14	,,	1·4	0·2	0·00016	0·04	34·43
15	,,	1·6	0·2	0·00016	0·04	37·50
16	,,	1·8	0·3	0·00024	0·06	40·30
17	,,	2·0	0·3	0·00024	0·06	42·86
18	,,	2·2	0·4	0·00032	0·08	45·20
19	,,	2·4	0·4	0·00032	0·08	47·37
20	,,	2·6	0·5	0·00040	0·10	49·37
21	,,	2·8	0·6	0·00048	0·12	51·22
22	,,	3·0	0·8	0·00064	0·16	52·94
23	,,	3·2	1·2	0·00096	0·24	54·55
24	,,	3·4	1·2	0·00096	0·24	56·04
25	,,	3·6	1·8	0·00144	0·36	57·45
26	,,	3·8	2·1	0·00168	0·42	58·76
27	,,	4·0	2·7	0·00216	0·54	60·00
28	,,	4·2	2·8	0·00234	0·56	61·17
29	,,	4·4	2·7	0·00216	0·54	62·26
30	,,	4·6	—	—	—	63·30
31	,,	4·8	2·8	0·00224	0·56	64·29
32	,,	5·0	2·7	0·00216	0·54	65·22
33	,,	5·2	2·8	0·00224	0·56	66·10
34	,,	5·4	2·9	0·00232	0·58	66·94
35	,,	5·6	2·9	0·00232	0·58	67·74
36	,,	5·8	3·0	0·00240	0·60	68·50
37	,,	6·0	2·9	0·00232	0·58	69·23
38	,,	6·2	2·9	0·00232	0·58	69·92
39	,,	6·4	2·9	0·00232	0·58	70·59
40	,,	6·6	2·8	0·00224	0·56	71·22
41	,,	6·8	2·8	0·00224	0·56	71·83
42	,,	7·0	2·9	0·00232	0·58	72·41
43	,,	7·2	3·0	0·00240	0·60	72·97
44	,,	7·4	3·0	0·00240	0·60	73·51
45	,,	7·6	3·1	0·00248	0·62	74·02
46	,,	7·8	3·2	0·00256	0·64	74·52
47	,,	8·0	3·2	0·00256	0·64	75·00

In using this method, the greatest possible care had to be taken that no trace of iodine might get into the bromide. For this reason, many of the earlier experiments, performed with commercially pure sodium bromide (giving no coloration with chlorine-water and starch-paste), were entirely spoiled. If iodine be present in the slightest traces, as it was in the experiments here referred to, the colour of the solution when mixed with sulphuric acid was slightly redder than that of the bromine-water, and it was quite impossible to get trustworthy results, all the results being far too high. This slight difference in colour was used in the later experiments as a most delicate test for iodine.

Experiments with stronger Hydrogen Bromide Solution.

5 c.c. of solution contains 1·62 grams HBr.

No. of experiment.	Volume of HBr. c.c.	Volume of H_2SO_4.	$Na_2S_2O_3$.	Br liberated.	Per cent. of HBr decomposed.	Per cent. of H_2SO_4.*
48	5	0·5	—	—	—	—
49	,,	0·9	—	—	—	—
50	,,	1·0	0·3	0·00024	0·027	27·27
51	,,	1·2	0·6	0·00048	0·054	31·03
52	,,	1·4	0·7	0·00056	0·062	34·43
53	,,	1·6	1·1	0·00088	0·097	37·50
54	,,	1·8	1·2	0·00096	0·106	40·30
55	,,	2·0	1·3	0·00104	0·115	42·86
56	,,	2·2	1·4	0·00112	0·125	45·20
57	,,	2·4	1·5	0·00120	0·133	47·37
58	,,	2·6	1·6	0·00128	0·142	49·37
59	,,	2·8	1·7	0·00136	0·151	51·22
60	,,	3·0	1·8	0·00144	0·160	52·94
61	,,	3·2	2·0	0·00160	0·177	54·55
62	,,	3·4	2·0	0·00160	0·177	56·04
63	,,	3·6	2·2	0·00176	0·195	57·45
64	,,	3·8	2·3	0·00184	0·207	58·76
65	,,	4·0	3·6	0·00288	0·323	60·00
66	,,	4·2	5·2	0·00416	0·467	61·17
67	,,	4·4	4·9	0·00392	0·440	62·26
68	,,	4·6	5·4	0·00432	0·485	63·30
69	,,	4·8	5·5	0·00440	0·494	64·29
70	,,	5·0	6·3	0·00504	0·566	65·22
71	,,	5·2	6·0	0·00480	0·539	66·10
72	,,	5·4	6·1	0·00488	0·548	66·94
73	,,	5·6	7·0	0·00560	0·628	67·74
74	,,	5·8	9·3	0·00744	0·835	68·50
75	,,	6·0	10·8	0·00864	1·212	69·23

* The percentages of sulphuric acid are not calculated out anew for the slight difference made by the stronger hydrobromic acid, and hence are only approximate in this table.

Experiments with Potassium Bromide.

5 c.c. of solution contains 1·19 grams KBr.

No. of experiment.	Volume of KBr solution.	Volume of H_2SO_4.	$Na_2S_2O_3$ required.	Br liberated.	Per cent. of HBr decomposed.	Per cent. of H_2SO_4 in solution.
	c.c.	c.c.				
76	5	1·0	—	—	—	—
77	,,	1·2	—	trace	—	—
78	,,	1·4	—	trace	—	—
79	,,	1·6	0·3	0·00024	0·03	—
80	,,	1·8	0·4	0·00032	0·04	—
81	,,	2·0	0·4	0·00032	0·04	—
82	,,	2·0	0·6	0·00048	0·06	—
83	,,	2·4	1·0	0·00080	0·10	—
84	,,	2·6	1·2	0·00096	0·12	—
85	,,	2·8	*	—	—	—
86	,,	3·0	*	—	—	—

Experiments with Sodium Bromide.

5 c.c. of solution contains 1·03 grams NaBr.

No of experiment.	Volume of NaBr solution.	Volume of H_2SO_4.	$Na_2S_2O_3$.	Br liberated.	Per cent. of HBr decomposed.	Per cent. of H_2SO_4 in solution.
	c.c.	c.c.				
87	5	0·5	—	—	—	—
88	,,	0·7	—	—	—	—
89	,,	1·0	—	—	—	26·90
90	,,	1·2	—	trace	—	30·63
91	,,	1·4	—	trace	—	34·00
92	,,	1·6	0·3	0·00024	0·03	36·27
93	,,	1·8	0·3	0·00024	0·03	39·85
94	,,	2·0	0·4	0·00032	0·04	42·40
95	,,	2·2	0·5	0·00040	0·05	44·74
96	,,	2·4	0·6	0·00048	0·06	46·90
97	,,	2·6	1·0	0·00080	0·10	48·32
98	,,	2·8	1·7	0·00136	0·17	50·70
99	,,	3·0	3·1	0·00248	0·31	52·47
100	,,	3·2	3·2	0·00256	0·32	54·08

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* In these two, crystals of potassium hydrogen sulphate began to form as soon as the solution cooled; this spoilt the experiment.

Experiments with Similar Proportions of Sulphuric Acid and Sodium Bromide variously diluted.

Each experiment is with 5 c.c. sodium bromide solution containing 1·03 grams NaBr.

No. of experiment.	Volume of H_2SO_4.	Volume of H_2O.	$Na_2S_2O_3$.	Br liberated.	Per cent. of Br decomposed.	Per cent. of H_2SO_4 in solution.
	c.c.	c.c.				
101	3·7	—	2·7	0·00216	0·27	59·01
102	,,	0·2	2·1	0·00168	0·21	58·00
103	,,	0·4	2·0	0·00160	0·20	57·03
104	,,	0·6	1·7	0·00136	0·17	56·09
105	,,	0·8	1·3	0·00104	0·13	55·17
106	,,	1·0	1·1	0·00088	0·11	54·20
107	,,	1·2	1·0	0·00080	0·10	53·45
108	,,	1·4	1·1	0·00088	0·11	52·62
109	,,	1·6	0·9	0·00072	0·09	51·82
110	,,	1·8	0·7	0·00056	0·07	51·04
111	,,	2·0	0·6	0·00048	0·06	50·29
112	,,	2·2	0·6	0·00048	0·06	49·56
113	1·84	—	0·3	0·00024	0·03	41·72
114	,,	0·2	0·3	0·00024	0·03	40·71
115	,,	0·4	0·2	0·00016	0·02	39·76
116	,,	0·6	0·3	0·00024	0·03	38·84
117	,,	0·8	0·2	0·00016	0·02	37·97
118	,,	1·0	0·2	0·00016	0·02	37·14
119	,,	1·2	0·2	0·00016	0·02	36·34
120	5·5	—	crystals	of $NaHSO_4$	formed.	68·13
121	,,	0·2	,,	,,	,,	67·24
122	,,	0·4	4·2	0·00336	0·42	66·36
123	,,	0·6	3·8	0·00304	0·38	65·50
124	,,	0·8	3·5	0·00280	0·35	64·66
125	,,	1·0	3·3	0·00264	0·33	63·85
126	,,	1·2	3·0	0·00240	0·30	63·05
127	,,	1·4	2·6	0·00208	0·26	62·26
128	,,	1·6	2·5	0·00200	0·25	61·52
129	,,	1·8	2·4	0·00192	0·24	60·77
130	,,	2·0	2·1	0·00168	0·21	60·06
131	,,	2·2	1·9	0·00152	0·19	59·35
132	,,	2·4	1·9	0·00152	0·19	58·67
133	,,	2·6	1·7	0·00136	0·17	57·99
134	,,	2·8	1·6	0·00128	0·16	57·34
135	,,	3·0	1·5	0·00120	0·15	56·68
136	,,	3·2	1·5	0·00120	0·15	56·07
137	,,	3·4	1·3	0·00104	0·13	55·45
138	,,	3·6	1·0	0·00080	0·10	54·85
139	,,	3·8	0·8	0·00064	0·08	54·26

In most of these experiments the sulphuric acid was in excess. With more concentrated hydrogen bromide solutions, a modification of this process must be used.

Experiments upon the action of sulphuric acid upon hydrogen bromide when the latter is in excess are now in progress.

VIII.—*On the α- and β-Modifications of Monochlorobenzene Hexachloride.*

By F. E. MATTHEWS, Ph.D.

THE existence of two isomeric modifications of benzene hexachloride having been definitely established (Trans., 1891, **59**, 167), it became of interest to see whether any benzene derivatives were capable of yielding isomeric modifications of the same character. The first substance selected for investigation was monochlorobenzene, but although two isomeric hexachlorides (heptachlorhexamethylenes), corresponding to the α- and β-benzene hexachlorides, have been isolated and identified, yet little fresh evidence has been furnished by them as to the constitution of these two types of substances.

It was shown in my previous paper that the benzene hexachlorides do not seem to admit of direct chlorination, and therefore, apparently, the only method of producing this class of substances is by the direct addition of chlorine to chlorine substitution products of benzene.

The monochlorobenzene used was obtained from Kahlbaum, and had evidently been prepared by the chlorination of benzene in the presence of iodine, as after being exposed to light for some time it became pink, owing to the separation of iodine. The presence of this small amount of iodine did not prevent the direct addition of 6 atoms of chlorine, but it probably facilitated the formation of substitution compounds and, as a matter of fact, a considerable amount of the substance was always converted into a heavy, oily, non-crystalline product; this, owing to the methods of purifying the hexachlorides adopted, was not preserved; in examining the action of bromine on the chlorobenzene under conditions similar to those in which benzene hexabromide is produced, no addition product was obtained, but parachlorobromobenzene was produced apparently free from other bromine compounds.* It seems probable that a better yield of the hexachlorides would have been obtained if no iodine had been present; and as benzene hexabromide takes much longer to form than the corresponding chloride, in the action of bromine on chlorobenzene, the iodine completely prevented the formation of the hexabromide.

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* The presence of iodine in the chlorobenzene was not observed till this work was considerably advanced, and as the hexachlorides could be produced in spite of the iodine, it did not seem worth while to recommence the work with a compound free from iodine.

Action of Chlorine in presence of Sodium Hydrate on Monochlorobenzene.

Some monochlorobenzene was placed in a flask, and covered with a dilute solution (1—2 per cent.) of sodium hydrate. A rapid stream of chlorine was passed into the mixture, and, for a considerable time, the whole of the chlorine was absorbed with the evolution of a considerable amount of heat. The under layer of chlorobenzene became bright-yellow, and could no longer be made to absorb any more chlorine. The flask was then placed outside the laboratory, and after some time the oily layer at the bottom became colourless, but without the deposition of any solid matter. It was noticed that the decolorisation of the chlorobenzene was greatly accelerated by exposure to direct sunlight, although heat alone did not appear to have any effect on the rapidity with which the action proceeded. The chlorobenzene had to be saturated with chlorine two or three times, and allowed to decolorise between each saturation, before any signs of crystallisation were apparent; sometimes hard crystals were obtained, which could be readily separated from the oily substance, whilst at other times the whole layer was transformed into a semi-solid, buttery mass from which the crystalline portion could be separated only with great difficulty. It was found that the best result was obtained when a considerable amount (150—200 grams) of chlorobenzene was acted on at once, and also that the crystals which were first deposited were harder and more readily purified than those obtained by the subsequent treatment of the separated oily portions.

The harder crystals could be readily separated from the oily matter by simple decantation, or filtration through coarse muslin; to obtain a solid from the buttery mass was a matter of considerable difficulty. Filtration through muslin removed a small amount of the oil, and heavy pressure between filter-paper continued for 24 hours got rid of a further portion, but better results were obtained by treating the mass, after pressure between filter-paper, with boiling light petroleum, by which the greater part of the oil could be removed with a very small loss of solid substance. When the crude mass was nearly free from oil, it did not fuse under boiling water, whilst the presence of a rather large amount of the oil caused it to melt rapidly under these conditions.

A chlorine determination was made on the crude substance after the greater part of the oily matter had been removed as above.

0·2556 gram of substance burnt with ignited Iceland spar gave 0·7764 gram AgCl.

	Theory for $C_6H_5Cl_7$.	Found.
Cl........	76·34 per cent.	75·15 per cent.

This analysis showed that the crude substance must be a hexachloride of chlorobenzene.

Separation of α- and β-Monochlorobenzene Hexachlorides.

On determining the melting point of the crude $C_6H_5Cl_7$ obtained from various preparations, it was found to melt anywhere between 70° and 140°, according to the amount of oily matter which had been removed from it. In all cases, however, a small residue remained unmelted, but this more infusible substance appeared much less than in the case of the corresponding benzene compound.

Fractional crystallisation was first tried for the separation of the substances, but good results could not be obtained by the use of any solvent, although the substance of higher melting point was always contained in greater proportion in the crystals first deposited. In one experiment, about 100 grams of crude $C_6H_5Cl_7$ was treated with cold absolute alcohol. A residue of less than 0·1 gram was finally obtained which showed no signs of melting at 210°. This was probably the β-compound in a state of approximate purity. Undoubtedly by means of a large number of fractional crystallisations from either alcohol, benzene, or light petroleum, a separation could be effected, but the process was abandoned as being unsatisfactory.

The process used by Meunier for the separation of α- and β-benzene hexachlorides was next tried, that is, to boil the crude product with alcoholic potassium cyanide for 30 hours, which, in the case of the benzene hexachlorides, only decomposes the α-compound. In the present case, this method of separation cannot be used, as although 40 grams of crude $C_6H_5Cl_7$ were taken for the experiment, no trace of the β-compound could be detected amongst the products of the reaction. The compounds $C_6H_5Cl_7$, which must contain 2 atoms of chlorine combined with the same atom of carbon, are not as stable as the corresponding compounds $C_6H_6Cl_6$.

Separation by steam-distillation was at last tried. This was found to answer better, but the process was very slow, as only about 1 gram per hour of substance came over and condensed in the receiver, and further the steam-distilled substance was not quite free from the β-compound. If 100 grams of the mixed substances be distilled with steam until only 1—2 grams of residue are left in the flask, the residue on recrystallisation is found to be the pure β-compound. The α-compound was obtained pure by recrystallising the steam-distillate several times from alcohol, benzene or light petroleum, and rejecting the first crop obtained by each recrystallisation.

A chlorine determination made with the α-chlorobenzene hexachloride purified as above gave the following result:—

0·2300 gram of substance, burnt with ignited Iceland spar, gave 0·7081 gram AgCl.

	Theory for $C_6H_5Cl_7$.	Found.
Cl........	76·34 per cent.	76·16 per cent.

A molecular weight determination by Raoult's method gave results as follows:—

Substance taken............	0·2041 gram.
Benzene solution	17·2096 grams.
Depression of freezing point..	0·18°.

	Theory for $C_6H_5Cl_7$.	Found.
Molecular weight	325·5	323

α-Monochlorobenzene hexachloride is a colourless, crystalline substance, which, when cold, possesses a not very strong but most persistent musty odour; when heated, its smell closely resembles that of α-benzene hexachloride. It is insoluble in water, but is moderately soluble in all the ordinary organic solvents, and especially so in benzene; it crystallises well from most of them, except acetic acid, from which it is frequently deposited in the form of an oil. It melts, when pure, at about 146°, but when mixed with more or less of the β-substance, that is, in some of the first crops obtained during its purification, the melting point may be as high as 160°. On carefully raising the temperature, the substance may be sublimed without decomposition, but if the heat be suddenly applied, it is largely broken up into $C_6H_2Cl_4$ [1 : 3 : 4 : 5] and hydrogen chloride.

On warming the substance, for a few minutes, to about 60°, with an alcoholic solution of either potassium or sodium hydrate, it is decomposed quantitatively according to the following equation:—

$$C_6H_5Cl_7 + 3KOH = C_6H_2Cl_4 + 3KCl + 3OH_2.$$

This was proved by the following experiment:—

0·4677 gram of pure substance was dissolved in 90 per cent. alcohol, an excess of sodium hydrate, prepared from sodium, was added, and the mixture gently warmed for a few minutes. Water was then added to the mixture, and the precipitated tetrachlorobenzene filtered off, and thoroughly washed. The filtrate was then titrated with decinormal silver nitrate solution (1 c.c. = 0·00352 gram Cl) and 43·6 c.c. of the standard solution was required to precipitate the chlorine.

	Calculated.	Found.
Chlorine in solution..	0·1537 gram.	0·1535 gram.

On long-continued boiling of an alcoholic solution of α-$C_6H_5Cl_7$ with zinc dust, six atoms of chlorine are removed with the reproduction of monochlorobenzene. The reaction will probably be of importance in determining the constitution of substances of this class.

α-Monochlorobenzene hexachloride is not acted on by strong sulphuric acid, and does not yield a nitro-compound with fuming nitric acid; up to the present, I have been unable to chlorinate it further.

β-Monochlorobenzene hexachloride has been previously obtained by Otto (*Annalen*, **141**, 101) by the action of chlorine upon sulphobenzide in sunlight. By the action of chlorine in presence of sodium hydrate upon monochlorobenzene, it is only produced in very small quantity.

The composition was determined by the following analysis:—

0·1728 gram of substance, burnt with ignited Iceland spar, gave 0·5387 gram AgCl.

	Theory for $C_6H_5Cl_7$.	Found.
Cl........	76·34 per cent.	77·12 per cent.

A molecular weight determination was made by Raoult's method, but although the result came out satisfactorily, yet the very slight depression of the freezing point renders the experiment somewhat untrustworthy, and, but for the close analogy with benzene hexachloride, could not by itself be depended upon.

Weight of substance taken ..	0·0833 gram.
Weight of benzene	17·7736 grams.
Depression of freezing point..	0·07°.

	Theory for $C_6H_5Cl_7$.	Found.
Molecular weight	325·5	328

β-Monochlorobenzene hexachloride crystallises from alcohol in small, but exceedingly lustrous crystals, which, in appearance, closely resemble β-benzene hexachloride. It is only slightly soluble in the ordinary organic solvents, so much so, that its molecular weight was only determined with difficulty in benzene solution, and could not be determined at all in acetic acid. It melts at about 260° (Otto, *loc. cit.*, 255—257), and can be sublimed undecomposed if carefully heated; on being more strongly heated, it evolves hydrogen chloride.

On heating with alcoholic potash for some time, it yields the same tetrachlorobenzene [1 : 3 : 4 : 5] as the α-substance. It is more stable towards alkalis than the corresponding α-compound, but is much more easily acted upon by them than β-benzene hexachloride. On account of the small amount of pure material obtained, the substance could not be further investigated.

It is interesting to notice that the displacement of one more atom of hydrogen by chlorine in α- and β-benzene hexachlorides lowers the melting point in both cases.

		M. p.		M. p.
$C_6H_6Cl_6$	α-	157°	β-	about 300°.
$C_6H_5Cl_7$	α-	146°	β-	„ 260°

Action of Alcoholic Potassium Cyanide on α-$C_6H_6Cl_6$ and on α- and β-$C_6H_5Cl_7$ (Meunier's Method of separating β- from α-$C_6H_6Cl_6$).

In the last paper, in describing the action of alcoholic potassium cyanide upon α-benzene hexachloride, the main reaction had not been discovered. The decomposition of crude monochlorobenzene hexachloride by alcoholic potassium cyanide has furnished the clue to the chief reaction which takes place. 40 grams of the crude hexachloride were boiled with a slight excess of alcoholic potassium cyanide for 30 hours. During the reaction, a small quantity of ammonium cyanide was deposited in the condenser. On distilling off the alcohol and water from the products of the reaction, a considerable amount of a pinkish solid substance collected in the condenser. On adding more water to the flask, and continuing the distillation, a further quantity of the same solid was deposited, in all about 16 grams. This deposit was recrystallised from alcohol, and was then at once recognised by its characteristic crystals, and also by its melting point and odour, as [1 : 3 : 4 : 5] tetrachlorobenzene.

On repeating the reaction with α-benzene hexachloride, a considerable yield of [1 : 2 : 4] $C_6H_3Cl_3$ was obtained;* it had been previously overlooked on account of its not crystallising at the ordinary temperature, from its extreme solubility in alcohol and the admixture of a considerable amount of a black, tarry matter.

The chief action of alcoholic potassium cyanide upon α-benzene hexachloride, &c., is expressed by the following equation:—

$$C_6H_6Cl_6 + 3KCN = C_6H_3Cl_3 + 3KCl + 3HCN:$$

that is, that the potassium cyanide chiefly plays the part of a very weak alkali.

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* Since this paper was written, Dr. H. G. Colman has informed me that α-benzene hexachloride is almost quantitatively decomposed into unsymmetrical trichlorobenzene by alcoholic potassium acetate at 130°.

Unsymmetrical Tetrachlorobenzene [1 : 3 : 4 : 5].

This substance has been obtained by several chemists, but from the various melting points given by different observers, it was of interest to see which was probably correct.

Otto (*Annalen*, **141**, 105), by the action of chlorine on sulphobenzide, obtained C_6H_5Cl, $C_6H_5Cl_7(\beta)$, and an oil which contained sulphur and gave no definite figures on analysis (from the figures given, the oil was probably a mixture of C_6H_5Cl and $(C_6H_5)_2SO_2$, together with 70—80 per cent. α-$C_6H_5Cl_7$). On decomposing this oil with alcoholic potash, he obtained $C_6H_2Cl_4$, apparently in the characteristic crystals which I have since observed, and he gives the melting point as 33°.

Ladenburg (*Annalen*, **172**, 344) gives 27—28° as the melting point.

Jungfleisch (*Zeit. für Chem.*, 1868, 468), by the action of chlorine on monochlorobenzene in sunlight and decomposition of the resulting product by alcoholic potash, obtained $C_6H_2Cl_4$, and assigns 35° as the melting point.

Beilstein and Kurbatow (*Annalen*, **192**, 237) obtained the substance from ordinary unsymmetrical trichloraniline by the replacement of NH_2 by Cl_2. They found that the $C_6H_2Cl_4$, thus prepared, melted at 50—51°.

I have prepared unsymmetrical tetrachlorobenzene by several reactions: from α-monochlorobenzene hexachloride by the action of potash, soda, and alcoholic potassium cyanide; from β-monochlorobenzene hexachloride by the action of alcoholic potash; and in all cases, after recrystallisation from alcohol, the product was deposited in the characteristic, double fan-shaped crystals described by Otto, and the melting point was invariably from 33° to 35°. This melting point was not raised by subsequent recrystallisation, and for some time I thought that there must be some mistake on Beilstein's part, as my results confirmed the observations of Otto, Ladenburg, and Jungfleisch; but after some time I found that the substance, after steam-distillation, melted about 2° higher than I had previously observed. On repeating this process several times, a melting point as high as 43° has been obtained, and, therefore, in all probability, the melting point given by Beilstein and Kurbatow, 50—51°, is correct. In all the methods of formation, except that of Beilstein and Kurbatow, there is probably some small amount of another substance present, which cannot be removed by fractional crystallisation.

That the substance I was working with was not very impure was shown by the following analysis and molecular weight determination:—

0·3546 gram substance, burnt with ignited Iceland spar, gave 0·9490 gram AgCl.

	Theory for $C_6H_2Cl_4$.	Found.
Cl........	65·74 per cent.	66·20 per cent.

Molecular weight determination:—

Weight of substance..........	0·2026 gram.
Weight of benzene	16·0538 grams.
Depression of freezing point....	0·31°.

	Theory for $C_6H_2Cl_4$.	Found.
Molecular weight	216	199·5

In order that there should be no doubt as to which tetrachlorobenzene is obtained by the abstraction of 3 mols. HCl from α- or β-monochlorobenzene hexachloride, the nitro-derivative was prepared; this, after being recrystallised from alcohol, melted at 23°. Beilstein (*Handbuch*, 2 ed., ii, 63) gives the melting point of $C_6HCl_4{\cdot}NO_2$ [1 : 3 : 4 : 5 : 2] as 21—22°. This shows conclusively that the same tetrachlorobenzene is obtained by decomposing α- and β-monochlorobenzene hexachloride, by alkalis as Beilstein and Kurbatow obtained from unsymmetrical trichloraniline.

Preparation of Benzene Hexabromide.

Some benzene was placed upon the surface of a dilute solution of sodium hydrate, and a stream of air, saturated with bromine, was let into the mixture for some time. After some hours, the benzene layer sank to the bottom of the flask, and, on continuing the treatment with bromine, crystals were at length formed.

A simpler method of preparing the hexabromide is to mix benzene and bromine together in the presence of water or of very dilute soda solution; the mixture of bromine and benzene falls to the bottom of the flask and, after some days, begins to deposit crystals, which can be readily separated from the liquid contents of the flask. The crystals, after being allowed to stand for some time on a porous plate, gave the following results on analysis:—

0·2429 gram, burnt with ignited Iceland spar, gave 0·4787 gram AgBr.

	Theory for $C_6H_6Br_6$.	Found.
Bromine......	86·0 per cent.	83·7 per cent.

This high percentage of bromine shows without doubt that benzene hexabromide is the main product of the reaction. I have not as yet further investigated the benzene hexabromide thus produced, but it will be of interest to see whether it is a simple substance or a mixture.

Meunier has already examined the hexabromide produced by other processes, and finds it to be homogeneous.

Action of Bromine on Monochlorobenzene.

On mixing chlorobenzene and bromine under water, and allowing the mixture to stand for about a week, a solid is produced which crystallises in plates which contain a small amount of interstitial bromine. If the mixture be allowed to stand for some weeks at the ordinary temperature of the laboratory, the whole of the bromine is used up, provided that the monochlorobenzene is in excess. The solid, on recrystallisation from alcohol, in the vapour of which it is exceedingly volatile, forms colourless, nacreous plates which melt at 65—66°. The substance appears to be parachlorobromobenzene, the melting point of which is given by Körner (*Jahresber.*, 1875, 319) as 67·4°.

A chlorine and bromine determination was made with the following result:—

0·1609 gram of the substance, burnt with ignited Iceland spar, gave 0·2639 gram of a mixture of AgCl and AgBr and 0·0090 gram of metallic silver.

0·2639 gram of the mixture of AgCl and AgBr was ignited in a stream of chlorine until the weight became constant, and gave 0·2291 gram AgCl.

	Found.	Theory.
Cl	18·93 per cent.	18·54 per cent.
Br	40·89 ,,	41·77 ,,

The molecular weight of the substance was also determined in benzene solution, in which it is extremely soluble.

0·3448 gram of the substance, dissolved in 17·9660 grams of benzene, caused a depression in the freezing point of 0·52°.

	Found.	Theory for C_6H_4ClBr.
Molecular weight	185	191·5

Theoretical Considerations.

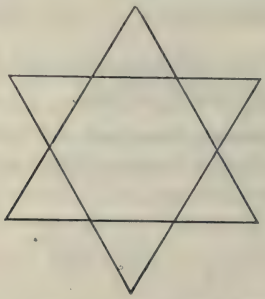
In the last paper, as no simpler explanation was then apparent, I hazarded the speculation that the reason for the existence of two isomeric modifications of benzene hexachloride, $C_6H_6Cl_6$, might be that, in one of the modifications, the 6 atoms of chlorine had become triad, and uniting with one another had formed a closed chain of 6 atoms of chlorine, the other modification containing 6 atoms of monad chlorine, and each atom being connected solely with 1 atom of carbon.

Since that time my attention has been called to a paper by Sachse (*Ber.*, **23**, 1363), "Ueber die geometrischen Isomerien der Hexamethylenederivate," which seems to afford a satisfactory explanation of the reason of the isomerism. This paper is extremely difficult to understand without the assistance of models, but with their aid is simplicity itself.

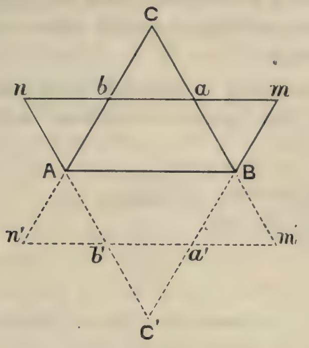
Sachse shows that there are two, and only two, positions in which the 6 carbon atoms of a hexamethylene ring can exist without being in a state of strain, the carbon atoms being assumed to be regular tetrahedra, and each tetrahedron being joined to its neighbour at a common vertex, so that the bases are parallel. (In the model this is effected by stringing each pair of adjacent tetrahedra upon a rigid rod, which passes through the centre point of the base and the apex of each tetrahedron. Thus the six tetrahedra are held together in the ring by six rigid rods.)

As I stated previously, it is difficult without models to describe the two fundamental forms of the hexamethylene ring, but my colleague Professor Minchin has kindly drawn up the following description of the two positions, which, I think, is quite intelligible.

1*st Form.*—On the side of a plane regular hexagon describe equilateral triangles all outwards from the area; on these triangles describe regular tetrahedra having the vertices, in alternate order, above and below the plane of the hexagon.



2*nd Form.*—Take an equilateral triangle ABC in a horizontal plane; bisect the sides BC, CA in *a* and *b*; on B*a* describe an equilateral triangle B*ma*, outwards, in the plane of the area ABC; on *a*C describe an equilateral triangle *a*C*b*, inwards; on *b*A describe one A*bn*, outwards; on these small equilateral triangles, in order, describe regular tetrahedra, having their vertices alternately below and above the plane of the area; take the image or reflection of the whole of this figure in the vertical plane containing the base AB; rotate the reflection ABC′ round AB until the *adjacent* faces of the tetrahedra at C and C′ become parallel to each other. The figure is then that of the second form.



(This description applies to the 1st form, if, instead of taking the direct image of the first equilateral triangle ABC with its tetrahedra, we take its inverted image, no rotation round AB being now necessary because the adjacent faces at C and C′ are at once parallel.)

Should Sachse's hypothesis prove to be correct, there can be little doubt that the, at present designated, β-modification, as possessing the higher melting point, will correspond with the symmetrical (1st) form of the hexamethylene ring, and that the α-modification will be represented by the unsymmetrical form.

In the case of the hexachlorides of benzene, according to Sachse's theory, only two modifications are possible, assuming that each atom of carbon is directly connected with 1 atom of chlorine; but in the case of the hexachlorides of chlorobenzene (monochloro-substitution products of α- and β-benzene hexachlorides), three modifications are theoretically possible. As in the 1st form of the hexamethylene ring the whole of the 6 carbon atoms are perfectly symmetrical, it is immaterial which of the 6 atoms of hydrogen in β-$C_6H_6Cl_6$ is substituted by chlorine to produce β-$C_6H_5Cl_7$. In the second form of the hexamethylene ring, however, the atoms of carbon are not all symmetrically arranged: four atoms [2, 3, 5, 6] are symmetrical, as are, likewise, 1 and 4. Therefore two α-derivatives, $C_6H_5Cl_7$, may be expected, and it appears likely that they would be exceedingly similar in their properties.

I have been unable to obtain α-monochlorobenzene hexachloride with a perfectly constant melting point, although convinced that the β-substance had been entirely separated, and it seems not unlikely that the α-compound here described may consist of a mixture of two theoretically possible substances which resemble one another so closely as to resist all the ordinary methods of separation.

It will be of considerable importance to see whether two isomeric hexamethylenes are capable of existence. According to Sachse's hypothesis, this should be the case, and the discovery of two isomeric modifications of hexamethylene would leave little or no doubt as to the truth of his theory.

I have been attempting to convert these chlorine derivatives into the hexamethylenes, but up to now without success. I am continuing the investigations.

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IX.—*Some Metallic Hydrosulphides.*

By S. E. Linder and Harold Picton.

Introduction.

The research took its rise in an observation made while drying some precipitated antimony sulphide. The substance, collected on a Gooch's crucible and well washed, was heated in a vessel with a bright copper lid, and it was observed that the copper lid was blackened. This appeared to be due to sulphuretted hydrogen, but as the sulphide had been well washed, such an explanation involved the assumption that the freshly precipitated sulphide was combined with sulphuretted hydrogen. This circumstance suggested an inquiry into the composition of the freshly precipitated sulphides. In spite of the amount of work done on the sulphides, very little is recorded of any investigation into the composition of the freshly precipitated compounds; it seemed worth while, therefore, to undertake such an investigation.

This research has opened up other inquiries on the physical side, which are of much interest, and have now become the main subject of our work. But before entering upon these, we propose, in this first paper, to review the purely chemical results arrived at in the course of our investigation. Unfortunately these are not so clearly definable as we could wish, the compounds dealt with being complicated and often unstable. The chief facts which the chemical portion of our work has revealed or extended may be shortly stated as follows.

The ordinary sulphide precipitates in most cases contain combined sulphuretted hydrogen.

In some cases, these precipitates appear to have a definite composition and to be stable compounds.

By other methods, higher hydrosulphides are occasionally obtainable. These are compounds of high molecular weight.

They undergo condensation with elimination of sulphuretted hydrogen under the influence of acids.

They form solutions of moderate strength.

Before entering upon our own work, we will briefly indicate what has already been done on this subject. We shall not refer to the hydrosulphides of the alkalis or the alkaline earth metals, as this portion of our work does not touch on these. With regard to other hydrosulphides, there is very little to be said. Thomsen (*Ber.*, **11**, 2044) found that zinc sulphate is completely precipitated by its equivalent of sodium hydrosulphide. On adding twice this quantity, he obtained an opalescent solution, which he concluded contained zinc hydrosulphide. Baubigny (*Compt. rend.*, **97**, 1417) found that, on passing sulphuretted hydrogen into a solution of zinc sulphate at 0°, he got a precipitate of zinc sulphide containing excess of sulphur. He found that the excess of sulphur in the precipitate varied. Just the same results were obtained in the case of nickel sulphate. V. v. Zotta qualifies Thomsen's results in a paper on the action of sodium hydrosulphide on zinc sulphate (*Monatsh.*, **10**, 807—812).

Among papers which have an indirect bearing on the subject, we may mention that of Clermont and Frommel (*Compt. rend.*, **87**, 330), who showed that, on continuously boiling certain sulphide precipitates with water, sulphuretted hydrogen is evolved; this they proved to be due to decomposition of the sulphide by the water. Examples are the sulphides of arsenic, iron, and antimony.

Winsinger and Spring have prepared metallic sulphide solutions by long continued washing of the precipitated sulphide with sulphuretted hydrogen water (*Bull. Soc. Chim.*, **49**, 452, and **48**, 166). Winsinger has also shown that certain metallic hydrates (*e.g.*, zinc) pass into solution on long continued treatment with sulphuretted hydrogen water. We were not acquainted with the later work of Winsinger and Spring when preparing the present paper, and thus arrived independently at similar methods of preparing these solutions.

Antony and Lucchesi made some experiments on the ordinary lead, copper, bismuth, antimony, and gold sulphide precipitates. Their precipitates were obtained in the ordinary way, washed with saturated sulphuretted hydrogen water, pressed between blotting paper, and dried at 120—130°. Under these circumstances, the precipitates, of course, contained mechanically adhering sulphuretted hydrogen, and the small quantity of sulphuretted hydrogen evolved and detected by means of silver nitrate was put down to this cause. The conclusion was, therefore, arrived at that the freshly precipitated compounds were the normal sulphides (*Gazzetta*, **19**, 545—562).

GENERAL STATEMENT.

Attention was first directed to the composition of the precipitates obtained in the ordinary way. The first result of our experiments was to prove that excess of sulphur was present in these precipitates; it was also found that the amount is not always constant. As in many cases the excess was small, the question naturally arose as to whether this could be free sulphur liberated during precipitation. To lessen the chances of such precipitation, boiled water was in many cases used. The only certain proof, however, was to make a searching examination in one of the cases where sulphur might most readily be expected to be formed; and for this purpose mercury sulphide was chosen; it gives a very small excess of sulphur and the liability to deposit sulphur unless due precautions are taken is well-known. The precipitate, after washing with alcohol, was carefully extracted with carbon bisulphide, but still yielded the same excess as before; and in order to obviate the objection that this extraction might be imperfect, another method more easily applied was used. This consisted in heating the precipitated compound in a current of hydrogen; in this way the sulphuretted hydrogen was driven off and absorbed by soda, and there was no longer any possibility of the excess being due to free sulphur. But though washed to all appearance perfectly free from sulphuretted hydrogen, it might yet perhaps be thought that some small quantity of the gas was mechanically retained in the interstices of the precipitate. As a final test, therefore, the precipitate, after complete washing, was extracted carefully with carbon bisulphide, washed free from every trace of carbon bisulphide, and then completely dried in a vacuum. The substance so dried still retained sulphuretted hydrogen, however, which was slowly given off on heating, and collected in soda. The same result was obtained in this case as in the others. The sulphur is, therefore, without any doubt *combined* with the freshly precipitated sulphide in the form of sulphuretted hydrogen.

What most influences the excess of sulphur seems to be the nature of the acid present. In many cases, however, it seems to vary according to no ascertainable rule, and in these cases it is, therefore, only possible to establish the main fact that a hydrosulphide of some kind is formed.

To ensure combination with the maximum amount of sulphuretted hydrogen, the neutral solutions of the metallic salts were allowed to run into excess of sulphuretted hydrogen water. In every case examined a solution clear by transmitted light was thus obtained. In many, but not all, cases this solution could be freed from its uncombined sulphuretted hydrogen by a current of hydrogen without causing precipitation. To these solutions attention was next directed. It was found that acids, unless present in small quantity, caused their precipitation, whilst the same effect was produced by the addition of metallic salts of inorganic acids. This property has long been made use of in the filtration of certain sulphides, for instance, tin sulphide. The salts of organic acids did not exert so powerful an action.

It is obvious that, according to this method of obtaining these solutions, an equivalent of acid was liberated by the action between sulphuretted hydrogen and the metallic salt. Now one of the difficulties which misled us in the early part of this work was the varying influence of different acids on the compounds formed. In the case of arsenic, for instance, the presence of hydrochloric acid does not appear to have any constant effect upon the product. With copper, however, variation in the nature of the acid present exerts a profound effect. A method was therefore sought in which the action of acids would be eliminated. The metallic hydrates or sulphides, suspended in water, were treated with sulphuretted hydrogen, solutions being thus obtained in some cases. These solutions are clear by transmitted light, though in the case of metals yielding black sulphides they are intensely dark. They are almost always strongly fluorescent, so that by reflected light they have a turbid appearance. Thus arsenic gives a solution which appears quite milky by reflected light, but by transmitted light has a clear, somewhat reddish-yellow colour. These neutral solutions are, like the others, precipitated by the addition of metallic salts.

It was proved by a blank experiment with sulphuretted hydrogen water that a current of hydrogen would completely expel dissolved sulphuretted hydrogen.

Experimental Methods.

All the reagents employed were very carefully tested for traces of sulphate. Thus no specimen of hydrochloric acid was employed which after dilution showed any sign of precipitate on the addition of barium chloride and allowing the mixture to stand over night.

Precipitates.—The precipitation was always carried on in a Drechsel's bottle, which could be tightly stoppered, and had two stopcocks sealed on to the side-tubes. In most cases, a measured quantity of the metallic solution was allowed to run into about 200 c.c. of saturated and acidified sulphuretted hydrogen water contained in the bottle; a rapid current of sulphuretted hydrogen was at the same time passed continuously through the water. The stopper was then introduced, sulphuretted hydrogen once more passed through the liquid, the stopcocks closed, and, where necessary, the solution allowed to stand until the precipitate had settled. We always took care to have an outward pressure of sulphuretted hydrogen.

The precipitate having settled, two different methods were adopted.

1. It was collected by filtering in the ordinary way and washed thoroughly with the washings of the Drechsel's bottle, the wash water being tested with lead acetate till free from sulphuretted hydrogen. The precipitate was then either washed off the filter into the original Drechsel's bottle, or filter-paper and precipitate were together dropped into it. Pure caustic soda was added, and some water. Chlorine was then passed through the liquid to saturation. It was next evaporated, treated several times with hydrochloric acid to destroy chlorate, filtered to retain any traces of residual sulphur, and precipitated with barium chloride. In several cases, traces of sulphur were thus obtained and oxidised with chlorate, but as a rule they yielded at most 2 or 3 milligrams of barium sulphate. The sulphate was collected on a Gooch's crucible. It has been stated that sulphuric acid is found in a liquid after evaporation on the water-bath; but on making a blank experiment and proceeding in exactly the same way as with our other experiments, only half a milligram of barium sulphate was obtained after two hours' evaporation. It is to be observed also that in these prolonged operations the tendency to loss of sulphur would more than counter-balance any such gain.

2. The precipitate was collected on a Gooch's crucible, and, after careful washing, introduced into an apparatus in which it could be heated in a current of hydrogen. In the first form of this apparatus a large, red caoutchouc stopper was used to close the mouth of the vessel in which the precipitate was heated. Owing to the curious behaviour of the precipitate under these conditions, and the immense time (several days) during which sulphuretted hydrogen continued to be evolved, the apparatus was carefully re-examined. It was found that the caoutchouc stopper, on heating, continuously evolved traces of sulphuretted hydrogen. The hydrogen entering the apparatus was quite free from sulphur. The cause of the above behaviour is not far to seek. Red caoutchouc is coloured with antimony sulphide, and this probably contains some combined sulphuretted hydrogen. It is the slow decomposition of the hydrosulphide on heating which causes the observed evolution of hydric sulphide. The form of apparatus afterwards used was the following:—The hydrogen passed through a column of solid lead acetate, through two U-tubes containing

alkaline lead acetate, and then through sulphuric acid. The vessel in which the sulphide was heated was closed with a well-ground glass stopper, having a thermometer ground into it. The issuing gas passed first over the surface of some strong potash solution contained in a small flask, which absorbed nearly all the sulphuretted hydrogen. This arrangement made it easy to test the issuing gas after a certain number of hours, without fear of loss, by withdrawing the tube and allowing the gas to impinge upon moistened lead acetate paper. The gas next passed through a small Drechsel's bottle containing caustic soda, and then through a U-tube containing the same liquid. The last never showed any trace of sulphide. The oxidation was carried on in the small Drechsel's bottle just as before. A calcium chloride bath was used to heat the apparatus.

Solutions from Metallic Salts.—The metallic solution was allowed to run into saturated sulphuretted hydrogen water just as with the precipitates. After closing the bottle, the liquid was re-saturated with sulphuretted hydrogen, and the dissolved gas then driven out by a current of hydrogen, purified by passing through two Woulffe's bottles containing alkaline lead acetate. The issuing gas was tested with lead acetate paper.

In a blank experiment, it was found that about 250 c.c. of sulphuretted hydrogen water could be thus freed from sulphuretted hydrogen in two hours. The reaction of the issuing gases affords an exceedingly delicate test for any sulphuretted hydrogen left in the liquid. Indeed, while the issuing gas still showed a decided reaction, the coloration produced by adding lead acetate to the liquid through which the gas was passing was such as indicated the presence of traces only of sulphuretted hydrogen. Where it is not possible to conduct the process so perfectly as to obtain absolutely *no* reaction with the issuing gases, it is still quite easy to see when the quantity of sulphuretted hydrogen left in the liquid has become far too small to affect the analytical results.

The solution, when thus freed from uncombined sulphuretted hydrogen, was treated with soda and oxidised as already described.

Solutions in Absence of Acid.—The metallic hydrate or sulphide was suspended in water and treated with sulphuretted hydrogen. When necessary, the bottle was left tightly stoppered to allow the action to be completed. The dissolved sulphuretted hydrogen was then, as before, driven out by a current of hydrogen.

Other methods besides those described were sometimes adopted, but these will be more conveniently considered in the individual cases. The details of the individual results, not many of which, unfortunately, are very definite, will next be given.

It should be observed that the principal experiments with each metal examined may be arranged under three heads:—

I. Examination of the reaction between the hydrate or sulphide and sulphuretted hydrogen.
II. Examination of the solutions formed in presence of the acid derived from the metallic salt.
III. Examination of the precipitated sulphide.

EXPERIMENTAL RESULTS.

Copper.

In the following experiments, a weighed quantity of pure copper sulphate was dissolved, made up to a given volume, and measured quantities of the solution used.

I. *Treatment of the Hydrate with Sulphuretted Hydrogen.*—A measured quantity of the copper solution was carefully precipitated with caustic soda, and the hydrate washed thoroughly till free from any trace of alkali or adherent salts. It was then washed into a Drechsel's bottle with boiled water, and treated with sulphuretted hydrogen.

Amount of crystallised copper sulphate used, 1·03084 grams.

The following are the amounts of barium sulphate obtained:—

a, 1·1072; *b*, 1·1096; *c*, 1·1044; calculated for CuS, 0·9642:

a. Treated with about 300 c.c. of water, sulphuretted hydrogen passed for 1 hour. Temperature, 11°; current of hydrogen passed for 1¾ hours. Partial solution.

b. Treated with about 400 c.c. of water. Sulphuretted hydrogen passed for 1½ hours. Cooled with ice throughout the experiment. Current of hydrogen passed for 2½ hours. Only a small part of the sulphide was dissolved.

c. Treated with about 400 c.c. of water. Saturated with sulphuretted hydrogen on Wednesday night. Left closely stoppered. Resaturated Thursday, Friday, and Saturday. By Monday an almost complete solution of the sulphide was obtained, only a few particles remaining undissolved. The dissolved sulphuretted hydrogen was then expelled by a current of hydrogen.

Taking the mean of the above results, we have:—

Sulphur found.	Calculated for $7CuS,H_2S$.
36·69 per cent.	36·59 per cent.

As the amount of precipitate and solution in the three cases varied, it is obvious that the precipitate obtained in this way has the same composition as the solution.

Precipitated copper sulphide, as might be expected from the above experiments, appears to form a solution when treated with sulphuretted hydrogen water.

II. *Precipitation in Presence of Acetic Acid.*—In the first attempts to get the precipitate in presence of acetic acid, copper sulphate was precipitated by caustic soda, and the hydrate redissolved by the addition of acetic acid. In this way, the presence of free sulphuric acid during the precipitation was avoided. The solution so obtained was allowed to run into sulphuretted hydrogen water, when a deep-brown solution was obtained; this, on standing, gradually deposited a precipitate. Great difficulty was experienced in obtaining this precipitate in a filterable form. Each solution was left from Thursday to Monday, and then filtered in an atmosphere of coal-gas.

The rapid oxidisability of copper sulphide made it necessary, especially in slow filtrations, to filter in absence of air. In these cases, the method of upward filtration was adopted. A small, perforated platinum disc was melted into one end of a short, wide piece of tubing. The other end was fitted with a cork, through which passed a tube connected with a filter-pump. A small piece of filter-paper was fitted over the platinum disc. After removing the stopper of the Drechsel's bottle, this small filter was lowered to the surface of the liquid, and the tube connected with the filter-pump. At the same time, a stream of coal gas was passed through the bottle, the mouth of which was plugged with cotton wool. This method is particularly adapted to the filtration of very fine precipitates.

In the two above cases, the filtration was exceedingly slow.

Copper sulphate taken, 1·0614 grams.

	$BaSO_4$ found.	Percentage of sulphur.
(1.)	1·1184 grams	36·13
(2.)	1·1245 ,,	36·28

These results cannot be entirely relied upon, owing to the time spent in filtration.

In another case a much easier plan was adopted, the sulphide solution being precipitated by the addition of ammonium chloride.

Copper sulphate taken, 0·5154 gram.

$BaSO_4$ found.	Percentage of sulphur.
0·5367 gram	36·00

The calculated percentage for $9CuS,H_2S$ is 35·96; and we thus see that the acid has begun its work of breaking down the hydrosulphide. The acid in this case acts in presence of excess of sulphuretted hydrogen, and evidently exercises its full influence at once, for the prolonged action in the two previous cases has at least not effected any further withdrawal of sulphuretted hydrogen. In each case, the solution was only very faintly acid when the reaction started.

III. *Solution in Presence of Acetic Acid.*—In these cases, the solution obtained in a similar way was freed from sulphuretted hydrogen by a current of hydrogen. They are therefore distinguished from the last, in that the acid was allowed to act upon the solution when not saturated with sulphuretted hydrogen. The following are the percentages of sulphur found :—

I.	II.	Mean.	Calculated for CuS.	Calculated for $22CuS,H_2S$.
34·67	34·56	34·61	33·65	34·61

The excess is here very small, and it is therefore impossible to assign a formula. The mean of the percentages is 34·61, and this agrees exactly with that calculated from $22CuS,H_2S$. But $21CuS,H_2S$ gives a percentage of 34·66, with a difference from the last formula of less than 0·2 per cent. on the total sulphur. It is only possible to say that a great molecular condensation has taken place.

IV. If precipitated in presence of hydrochloric acid, still further loss of sulphuretted hydrogen occurs, the excess of sulphur amounting to about 2 per cent. on the normal quantity, or, if a large amount of acid be added, to about 1 per cent.

The following numbers give the excesses on each 1·000 gram of calculated baric sulphate :—*a*, 0·027 : *b*, 0·018, and *c*, 0·014.

a. Precipitated in presence of a few drops of hydrochloric acid. Excess driven off by heat.

b. 4 drops of dilute sulphuric acid added. The precipitate collected on a Gooch's crucible, and excess of sulphuretted hydrogen driven off in a current of hydrogen.

c. Soda added to copper sulphate, and then excess of hydrochloric acid to redissolve the hydrate. Very acid with hydrochloric acid.

Several other methods were tried with copper with a view to obtaining a higher hydrosulphide, but without any definite result. The following may, however, be mentioned :—

V. Copper sulphate was treated with sodium hydrosulphide. A solution of copper sulphate was allowed to run into a solution of sodium hydrosulphide. This method seemed convenient on account of the immediate precipitation caused by the sodium sulphate formed. But much lower results were obtained than by the hydrate method, and the experiments were therefore abandoned. $BaSO_4$ found 0·8598 gram, calculated 0·7944; excess per cent. 8·23. The precipitate obtained in presence of acetic acid, by adding ammonium chloride, gave an excess of 11·32 per cent. (see above).

VI. As the solutions of antimony and arsenic in acid potassium tartrate are not precipitated by sulphuretted hydrogen, it was at first determined to use the same method for the copper solutions. The sulphate was precipitated with soda, acid potassium tartrate added, and the liquid made faintly acid with tartaric acid. The solution so obtained was allowed to run into sulphuretted hydrogen water; the excess was then driven out from the dark solution of copper with hydrogen. This method gave results similar to those obtained by precipitation in presence of acetic acid. But the results are not so concordant. Percentages of sulphur obtained: 36·10, 36·52.

VII. It was thought that, as the presence of water might have some effect in breaking down the hydrosulphide, some other liquid might be used; experiments, which bore no fruit, were carried out with two liquids—glycerine and ether. In the second case the copper sulphate was precipitated by soda, and the hydrate washed with warm water, then with alcohol, and finally with ether. The precipitate was washed into a Drechsel's bottle with dried ether, cooled with ice, and treated with a current of sulphuretted hydrogen. It was found impossible to get the hydrate completely acted on. Thus in two experiments when the calculated amount of barium sulphate was 0·9573 gram, that actually found was 0·7570 and 0·7875. Similar experiments were also made with glycerine, but without success.

Conclusion.—From the above experiments on copper sulphide we may conclude that, starting with the hydrosulphide $7CuS,H_2S$, this is broken down by the action of acids through successive stages expressible more or less approximately by the formulæ $9CuS,H_2S$ and $22CuS,H_2S$, till we finally arrive at a molecule composed of $(CuS)_n$ alone. This will probably be a higher multiple than 22CuS, a result tending to confirm the other proofs of the complex nature of the sulphides.

Mercury.

Pure mercuric chloride was used in these experiments.

I. *Treatment of Mercuric Sulphide with Sulphuretted Hydrogen.*—It was found that when washed mercuric sulphide is treated with sulphuretted hydrogen water, it is completely dissolved with formation of a deep brown solution. This seemed a convenient method of preparing the hydrosulphide in absence of acid.

1. 50 c.c. of mercuric chloride solution were taken, mixed with 100 c.c. of boiled water in a Drechsel's bottle, and 3 or 4 drops of hydrochloric acid added. A rapid current of sulphuretted hydrogen was passed through the liquid, which was then quickly filtered. The washed precipitate was treated with 250 c.c. of boiled water and sulphuretted hydrogen for 45 minutes. It was then cooled with ice, and the current of sulphuretted hydrogen passed for 15 minutes more, by which time complete solution was obtained. A current of hydrogen was next passed through the liquid, while still surrounded with ice, and it was quite free from sulphuretted hydrogen in 2½ hours.

2. 50 c.c. of mercuric chloride solution were acidified with 2 drops of hydrochloric acid. The liquid was boiled, cooled, and allowed to run into saturated sulphuretted hydrogen water (for which boiled water had been used). The precipitation was completed by the addition of 2 more drops of acid. The liquid was filtered, and the precipitate redissolved in boiled water by passing in sulphuretted hydrogen. The dissolved sulphuretted hydrogen was expelled by a current of hydrogen in about 2½ hours, no ice being, in this case, used.

Weight of mercury chloride taken, 1·00464 grams.

$BaSO_4$ found.	$BaSO_4$ calculated for HgS.
a. 0·8916 gram.	0·8375 gram.
b. 0·8910 ,,	—

Sulphur found.	Sulphur calculated for $31HgS,H_2S$.
14·166 per cent.	14·171 per cent.

The excess of sulphur found is small, being about 3 per cent. on the normal quantity. It is impossible to lay stress on so complex a formula.

The action of sulphuretted hydrogen on the precipitated sulphide is of considerable interest. It does not seem to depend on agitation of the liquid, though this, of course, aids solution. Washed mercuric sulphide left in contact with sulphuretted hydrogen water will show signs of solution after about half an hour. It is particularly noteworthy that mercuric sulphide, after *boiling* with water, is still capable of thus being acted upon by sulphuretted hydrogen. After *drying* at 100°, it loses this capacity.

II. *Mercury Precipitates in Presence of Acid.*—In these cases, the sulphide was precipitated from the chloride, sometimes with, sometimes without, the addition of acid. The precipitate thus obtained contains so small an amount of combined sulphuretted hydrogen that it was necessary to have very complete proof of its existence. In the general statement of results, the examination of this sulphide has been referred to. It is only necessary to add here that the product, though evidently of great molecular complexity, appears on the evidence to be a definite compound. It has yielded concordant results, and possesses very remarkable stability. Thus, when precipitated at 65°, it still retains its original composition. It withstood extraction with carbon bisulphide, and the prolonged washings with water and alcohol which this entailed. It also withstood drying in a vacuum, and when subsequently heated in a stream of pure hydrogen at 105°, took more than 15 hours to lose the whole of its very small quantity of combined sulphuretted hydrogen.

The following is a description of the methods employed in each experiment, the numerical results being given below :—

1. 100 c.c. of the boiled solution were allowed to run into 100 c.c. of sulphuretted hydrogen water kept at 65°. The precipitate was washed twice with water at 65° and once with water at 10°.

2. 100 c.c. of the boiled solution acidified with 1 drop of acid were allowed to run into 100 c.c. of saturated sulphuretted hydrogen water. Temperature 7°.

3. Precipitated in the ordinary way by passing sulphuretted hydrogen through the solution. The precipitate was extracted with carbon bisulphide. In extracting the wet precipitates, we washed first with alcohol, and then with a mixture of alcohol and amyl alcohol, which mixes very readily both with water and carbon bisulphide. This is much more satisfactory than the use of alcohol and ether. This experiment shows that the same compound is formed on passing sulphuretted hydrogen through the solution of mercuric chloride as when the latter is allowed to run into sulphuretted hydrogen water.

4. 100 c.c. of mercuric chloride solution acidified with 2 drops of hydrochloric acid were allowed to run into 100 c.c. of sulphuretted hydrogen. All the liquids had been boiled. A solution was at first formed, but soon deposited mercuric sulphide. The filtration was conducted in coal gas according to the method described under copper. Temperature of precipitation, 11°.

5. In this experiment, it was resolved to submit the precipitate to every possible test, in order to remove every shadow of doubt of its containing combined sulphuretted hydrogen. The precipitate was collected in a Gooch's crucible. It was first washed free from sulphuretted hydrogen with water, then washed in succession with absolute alcohol, and next with a mixture of ethyl and amyl alcohols, treated first two or three times with carbon bisulphide, with which it was allowed to remain in contact, and finally washed completely free

from carbon bisulphide with alcohol and amyl alcohol. The alcohol was then almost entirely removed by suction. The crucible was next placed in a desiccator, which was exhausted by means of a good filter-pump; after an hour or two, the precipitate was quite dry, and was weighed. The weight of substance was found to be 1·5285 grams.*

The crucible was then introduced into the heating apparatus, and heated for from 15 to 20 hours. After heating, the mercuric sulphide left was weighed. On the particular solution used, the calculated amount was 1·5226 grams; found, 1·5190 grams.

6. In this case, the wet sulphide was dried in hydrogen. The loss of sulphuretted hydrogen was much more rapid, and seems to be greatly aided by the water present. No more sulphuretted hydrogen was evolved after 2½ hours' heating. The mercuric sulphide was in this case also weighed. Calculated, 1·3476 grams; found, 1·3444 grams.

7. In this experiment also, the sulphide was dried in a current of hydrogen. The sulphide was probably not so moist, and took longer to lose its sulphuretted hydrogen. The time of heating was 8 hours.

In the numbers given below, the normal amount of barium sulphate calculated for HgS is added on to the excesses obtained in those experiments where the hydrosulphide was heated in hydrogen. For the sake of comparison, they are all reduced to quantities obtainable from the same same solution of mercuric chloride, though, as a matter of fact, the experiments were done on different solutions:—

$BaSO_4$ calculated for HgS, 1·6678 grams; found:—

(1.) 1·6906
(2.) 1·6917
(3.) 1·6956
(4.) 1·6916
(5.) 1·6961
(6.) 1·6926
(7.) 1·6904

It may be pointed out that in Experiment 5, we have guarded against the criticism that, on heating the wet sulphide, sulphuretted hydrogen might be evolved by its reaction with water. For in this case the sulphide was already dry, but when heated in dry hydrogen, continued to give off sulphuretted hydrogen for about 17 hours.

From the above numbers we see that the excess of sulphur found is about 1½ per cent. on the total quantity calculated for HgS. It is of course impossible to assign a formula to such a compound, but its approximate composition and relation to the higher hydrosulphide, already discussed, may be remembered from the formula $62HgS,H_2S$.

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* In another experiment on the same amount, which was not concluded, the weight of substance found was 1·5275 grams.

III. Some experiments were made with a view to obtain the mercury hydrosulphide solution in presence of acid. The mercuric chloride solution was allowed to run into considerable excess of sulphuretted hydrogen water. On passing a current of hydrogen through this liquid, however, the sulphide was usually precipitated, and the results were not concordant.

Conclusion.—The above experiments with mercury, like those with copper, suggest a very complicated formula for the molecule of mercuric sulphide. Indeed, supposing the precipitate to be a definite compound, the molecule $(HgS)_n$ must have a value for n certainly not lower than 62.

Arsenic.

In this case, after a great many trials, and the use of various methods, all attempts to obtain definite or concordant results had to be abandoned. The fact is, however, established that arsenic trisulphide does combine with sulphuretted hydrogen, although the amount is very small and the product is of varying composition.

I. *Solution in Absence of Acid.*—For this purpose arsenious acid is dissolved in hydrogen potassium tartrate, and the liquid treated with sulphuretted hydrogen. When fairly dilute, a perfectly clear solution is obtained, which is highly fluorescent. This was freed from sulphuretted hydrogen by a current of hydrogen as in the other cases. Soda was added, and the sulphide oxidised by chlorine.

	$BaSO_4$ found.	$BaSO_4$ calculated.	Excess per cent.
(1.)	2·6526 grams.	2·5612 grams.	3·6
(2.)	2·6365 „	2·5612 „	2·9
(3.)	2·8776 „	2·8249 „	1·8
(4.)	2·9113 „	2·8249 „	3·6

In 1 and 2 a solution was used containing 1·8137 grams of arsenious oxide in 500 c.c.; 200 c.c. of this were used in each experiment. In 3 and 4, 4·0011 grams of arsenious oxide are dissolved in 500 c.c. of water, and 100 c.c. used in each experiment.

Some of the hydrosulphide solution was boiled without producing any precipitation. The boiling was continued till no appreciable quantity of sulphuretted hydrogen was evolved. The analysis gave a result too low for As_2S_3. (Compare the work of Clermont and Frommel mentioned in the Introduction).

II. *Solution in Presence of Hydrochloric Acid.*—In these experiments arsenious acid was dissolved in soda, the solution made slightly acid with hydrochloric acid, and then allowed to run into sulphuretted hydrogen water. 100 c.c. of the arsenic solution was allowed to run into sulphuretted hydrogen water, and a current of hydrogen was then passed through the solution for 3½ hours.

	$BaSO_4$ found.	$BaSO_4$ calculated.	Excess per cent.
(1.)	3·1600 grams.	2·9126 grams.	4·6
(2.)	1·8832 „	1·8170 „	3·6

III. *Precipitate in Presence of Acetic Acid.*—Arsenious acid was dissolved in soda and made acid with acetic acid, then precipitated by sulphuretted hydrogen.

	$BaSO_4$ found.	$BaSO_4$ calculated.	Excess per cent.
(1.)	6·4072 grams.	6·1351 grams.	4·4

IV. *Precipitate in Presence of Hydrochloric Acid.*—The arsenite was in these cases acidified with hydrochloric acid sufficient to bring about precipitation.

	$BaSO_4$ found.	$BaSO_4$ calculated.	Excess per cent.
(1.)	1·2522 grams.	1·2158 grams.	2·9
(2.)	1·3996 „	1·3726 „	1·9
(3.)	2·9661 „	2·9126 „	1·8
(4.)	2·6817 „	2·6538 „	1·1
(5.)	1·8600 „	1·8170 „	2·4
(6.)	2·7112 „	2·6538 „	2·2

In Experiment 6, the arsenic was precipitated from acid solution by calcium chloride. In 4, the arsenic was allowed to run into sulphuretted hydrogen water, hydrochloric acid added to cause precipitation, about 1 c.c. of acid being used, and the precipitate collected on a Gooch's crucible. It was then heated in a current of hydrogen. At the end of 3¼ hours, all evolution of sulphuretted hydrogen had ceased. The large amount of acid probably lowered the result. Weight of sulphide after heating, 0·9370 gram. Calculated for As_2S_3, 0·9340 gram. In Experiment 5, the sulphide was collected on filter paper, and then dried in a current of hydrogen.

To see whether the compound would retain its sulphuretted hydrogen, some of the sulphide was dried in a vacuum. Final weight, 0·9415 gram. It was heated at 115°, when sulphuretted hydrogen was evolved, the precipitate losing 4 milligrams in weight. Weight of sulphide obtained, 0·9375 gram; calculated, 0·9340 gram.

Conclusion.—The formula about which the composition of the arsenic solutions oscillates is $8As_2S_3,H_2S$, which gives an excess of sulphur of a little over 4 per cent. The approximate formula for the precipitates in presence of hydrochloric acid will thus be $16As_2S_3,H_2S$.

Cadmium.

Pure cadmium oxide was obtained by igniting the carbonate. This was dissolved in hydrochloric acid and made up to a known volume.

I. *Treatment of the Hydrate with Sulphuretted Hydrogen.*—It has not yet been found possible to get the hydrate completely acted on by sulphuretted hydrogen. But the experience with zinc has shown that in these cases all depends on the state in which the hydrate is precipitated.

In the experiments made with cadmium, the precipitation of the hydrate was effected by adding sodium hydrate to the cadmium solution. A qualitative experiment was made by allowing the cadmium solution to run into caustic soda. The hydrate so obtained was treated with sulphuretted hydrogen water cooled by ice. It was only very partially dissolved after long standing.

The sulphide is not soluble in sulphuretted hydrogen water to any noteworthy extent.

II. The neutralised solution was allowed to run into sulphuretted hydrogen water. A yellow, fluorescent solution was obtained, but when this was freed from dissolved sulphuretted hydrogen by a current of hydrogen, it always deposited a precipitate, and no analysis of the solution could thus be obtained.

III. The precipitates obtained by two different methods gave concordant results, though the excess of sulphuretted hydrogen is small.

1. 100 c.c. of the cadmium solution were allowed to run into sulphuretted hydrogen water. A solution of the hydrosulphide was thus obtained, and was precipitated by the addition of ammonium chloride. It was then filtered through a Gooch's crucible, and heated in the apparatus above described. In this case, the precipitate was probably fairly dry, owing to the suction of the filter-pump. Sulphuretted hydrogen only ceased being evolved after heating for 20 hours.

2. 100 c.c. were diluted to about 200 c.c. and precipitated directly by passing a current of sulphuretted hydrogen through the solution slightly acid with hydrochloric acid. The sulphide was here also collected on a crucible, and dried in a current of hydrogen. The drying in this case occupied only about 1½ hours. The sulphide left was weighed. Found, 0·5926 gram; calculated, 0·5923 gram.

	Cadmium oxide taken.	Calculated $BaSO_4$.	Excess $BaSO_4$.
(1.)	0·5265 gram.	0·9584 gram.	0·0429 gram.
(2.)	0·5265 ,,	0·9584 ,,	0·0427 ,,

This gives an excess of 4·47 per cent. on the total calculated sulphur. This corresponds with the formula $22CdS,H_2S$, which, however, is nothing more than a convenient way of expressing percentage composition.

Zinc.

Crystallised zinc sulphate was powdered and dried at 110° till its weight was constant. The zinc sulphate was then weighed as the hydrate $ZnSO_4,H_2O$.

I. *Treatment of Zinc Hydrate with Sulphuretted Hydrogen.*—This has not afforded constant results. In the first experiments, the hydrate was precipitated by adding soda to the zinc sulphate solution till it was just alkaline. The hydrate, after careful washing, was treated with sulphuretted hydrogen and water.

1. In this case, the hydrate was left for a few hours in contact with sulphuretted hydrogen, the solution being cooled with ice.

$BaSO_4$ found.	Calculated.	Excess per cent.
1·4786 grams.	1·2870 grams.	14·7

2. In one case, when the hydrate was very carefully precipitated, it came down in a very gelatinous condition, and on treatment in ice with sulphuretted hydrogen water, it dissolved completely in a few hours, forming a solution clear by transmitted light, but by reflected light having a slightly bluish opalescence. On passing a current of hydrogen through this, however, it was precipitated.

Weight of zinc oxide used, 0·6639 gram.

$BaSO_4$ found.	Calculated.	Excess per cent.
0·9420 gram.	0·8642 gram	9·0

3. A number of ineffectual attempts were made to re-obtain this soluble hydrate. In one case, the carefully precipitated hydrate was treated with sulphuretted hydrogen water in ice, and then left all night surrounded with ice. Next day it was re-saturated with sulphuretted hydrogen. No solution was formed, and the sulphuretted hydrogen was then expelled by a current of hydrogen in 2½ hours.

$BaSO_4$ found.	$BaSO_4$ calculated.	Excess per cent.
0·7587 gram.	0·6592 gram.	13·0

A new method was sought for obtaining the translucent hydrate, and the following mode of procedure was found to answer best:—The solution of zinc is allowed to run into excess of caustic soda, by which it is completely dissolved. The excess of soda is now neutralised by adding dilute hydrochloric acid, whereupon the zinc hydrate is precipitated in a very gelatinous and translucent condition. The precipitate is readily washed free from adherent salts. The complete absence of sulphate in the washed hydrate was shown by dissolving it in hydrochloric acid, and testing with baric chloride; no trace of precipitate was obtained. To prepare the gelatinous hydrate, it is advisable not to operate with large quantities of zinc salt at one time. *Slow* precipitation only produces a more granular precipitate.

4. 50 c.c. of a different solution were, in this case, allowed to run into caustic soda. The precipitate obtained as above described was washed completely free from sulphate and chloride, and then washed off the filter-paper into a Drechsel's bottle. The residual zinc, including that in the filtrate from the hydrate, was estimated. The hydrate was treated with 300 c.c. of water and sulphuretted hydrogen, after cooling with ice. It did not dissolve the same day, but was left in ice over night. By next morning it had dissolved to a clear solution, having by reflected light somewhat the appearance of a filtered starch solution. A current of hydrogen was passed through the solution for 3½ hours; by this time there was only a very feeble reaction for sulphuretted hydrogen in the issuing gas, certainly not sufficient to indicate an appreciable amount of dissolved gas in the liquid. The solution still remained perfectly clear. The sulphur was oxidised in the usual way.

$BaSO_4$ found.	$BaSO_4$ calculated.	Excess per cent.
0·2811 gram.	0·2485 gram.	12·9

5. In another case a nearly complete solution of the hydrosulphide was obtained.

$BaSO_4$ found.	$BaSO_4$ calculated.	Excess per cent.
0·2982 gram.	0·2589 gram.	15

Precipitated zinc sulphide retains combined water, and the compound formed in the present case is, therefore, probably a hydroxy-hydrosulphide. It is impossible to give a definite formula to this hydrosulphide, but its composition is approximately that of $7ZnS,H_2S$. Copper, it will be remembered, gave the definite hydrosulphide $7CuS,H_2S$.

II. *Precipitate in Presence of Acid.*—Zinc was precipitated in presence of acetic acid.

	$BaSO_4$ found.	$BaSO_4$ calculated.
(1.)	0·4961 gram.	0·4594 gram.
(2.)	0·4961 ,,	0·4594 ,,

This yields about 8 per cent. excess, or expressing it by a formula—

Sulphur found.	Sulphur calculated for $12ZnS,H_2S$.
34·7 per cent.	35·6

The agreement with this formula is far closer than with any other simple one.

Precipitated zinc sulphide is known to contain combined water. The composition of the air-dried precipitate is given as $3ZnS,2H_2O$. According to this, the precipitated sulphide would have the formula $12ZnS,H_2S,6H_2O$.*

Bismuth.

With this metal, we have obtained no evidence of the formation of any hydrosulphide.

I. *Treatment of Hydrate with Sulphuretted Hydrogen.*—Pure bismuth oxide was dissolved in nitric acid, and the nitrate allowed to run into strong ammonia. The hydrate so obtained did not contain any nitrate. It was treated with water and sulphuretted hydrogen, and left for six days in a closely-stoppered bottle. One sample so obtained gave about 0·5 per cent. excess on the total sulphur.

Another was collected in a crucible, and heated in hydrogen. No sulphuretted hydrogen was evolved, the soda, on oxidation, containing no trace of sulphate.

The product of this reaction seems, therefore, to be Bi_2S_3.

II. *Bismuth Precipitates.*—A solution of bismuth chloride was treated with sulphuretted hydrogen, and the precipitate so obtained oxidised.

	$BaSO_4$ found.	$BaSO_4$ calculated.	Excess per cent.
(1.)	0·8735 gram.	0·8775 gram.	0
(2.)	0·8738 ,,	0·8775 ,,	0

It is thus evident that the bismuth sulphide is precipitated, quite uncombined with any sulphuretted hydrogen. It was at first thought that the large amount of acid necessarily present might account for this result, but the results obtained with the hydrate do not confirm that suspicion.

Silver.

No method of preparing a definite hydrosulphide in the case of silver has been found.

I. *Treatment of the Hydrate.*—It has been shown by Carnelley and Walker that silver hydrate, AgOH, is stable up to a temperature of 100°. We, therefore, decided to try the action of sulphuretted hydrogen on the freshly-precipitated hydrate. But even after very prolonged treatment the resulting compound did not show a percentage of sulphur perceptibly higher than that required for Ag_2S.

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* This formula makes allowance for the loss of weight due to sulphuretted hydrogen, and reckoned as water in earlier experiments.

1. Left from Thursday till Monday in contact with sulphuretted hydrogen water.
2. Left from Friday till Monday in contact with sulphuretted hydrogen water.
3. Left six weeks in contact with sulphuretted hydrogen water.
4. Left four weeks in contact with sulphuretted hydrogen water.

	$BaSO_4$ found.	$BaSO_4$ calculated.
(1.)	0·9697 gram.	0·9647 gram.
(2.)	1·0704 ,,	1·0855 ,,
(3.)	0·7346 ,,	0·7265 ,,
(4.)	0·9919 ,,	0·9836 ,,

The final reaction between silver hydrate and sulphuretted hydrogen seems, therefore, to consist in the formation of the sulphide, Ag_2S. It may be noted that these experiments show that, even on prolonged treatment, the precipitation of any noticeable amount of sulphur can be avoided.

II. *Silver Solutions.*—1. Sodium acetate was added to the silver nitrate solution, to prevent the liberation of nitric acid. 50 c.c. of the solution was boiled, and, on cooling, allowed to run into saturated sulphuretted hydrogen water, prepared from boiled water. The sulphuretted hydrogen was then driven out by a current of hydrogen.

2. 50 c.c. of silver nitrate solution were allowed to run into sulphuretted hydrogen water.

	$BaSO_4$ found.	$BaSO_4$ calculated.	Excess per cent.
(1.)	0·5100 gram.	0·4718 gram.	8·1
(2.)	0·5159 ,,	0·4981 ,,	3·6

III. *Precipitates.*—All that can be said about the silver precipitates is that they contain sulphuretted hydrogen. Thus, in one case, we had $BaSO_4$ found, 0·4625 gram; calculated, 0·4112 gram.

Antimony.

With antimony, as with arsenic, it has proved impossible to obtain very definite results. The sulphide retains a small but unmistakable amount of combined sulphuretted hydrogen.

I. *Neutral.*—In these experiments, a solution of tartar emetic was used, and, after saturation with sulphuretted hydrogen was treated with a current of hydrogen. The sulphide was oxidised in the usual way. After evaporation on the water-bath, a precipitate of barium chloride was filtered off. This was always examined for sulphur or basic sulphate, of which it sometimes contained traces.

Before precipitation with barium chloride, the antimony was deposited on platinum. This was found to be absolutely necessary, the barium sulphate exhibiting an invincible tendency to carry down large quantities of antimony, which could only be extracted from it by fusion with soda.

1. Solution of the sulphide, obtained as above.

2. Precipitate obtained from the neutral sulphide solution by addition of calcic chloride.

	$BaSO_4$ found.	$BaSO_4$ calculated.	Excess per cent.
(1.)	1·1858 grams.	1·1608 grams.	2·1
(2.)	0·641 „	0·627 „	2·2

Prolonged treatment of antimony sulphide with sulphuretted hydrogen water did not effect any solution.

II. *In Presence of Acid.*—1. 100 c.c. of tartar emetic solution was allowed to run into sulphuretted hydrogen water acid with acetic acid. The precipitation was completed by the addition of ammonium chloride. The barium sulphate obtained was fused with soda. Only a trace of antimony (which had escaped precipitation) was discovered in it.

2. A similar experiment; but in this case the barium sulphate contained no trace of antimony.

	$BaSO_4$ found.	$BaSO_4$ calculated.	Excess per cent.
(1.)	0·8974 gram.	0·8600 gram.	4·4
(2.)	0·9028 „	0·8600 „	4·9

It is curious that in this case a higher hydrosulphide seems to be formed in presence of acid.

To confirm the presence of combined sulphuretted hydrogen, some of the sulphide, after careful washing, was treated with absolute alcohol on a Gooch's crucible and then heated. Owing to a defect in the apparatus, the experiment could not be made quantitative, but the sulphide continued to give off sulphuretted hydrogen for several hours.

Indium.

It was found very difficult to deal with the sulphide of this metal, but the following experiment is worthy of note.

Indium oxide was dissolved in hydrochloric acid, precipitated by ammonia, and the hydrate treated with sulphuretted hydrogen.

For 10 *minutes the colour remained white;* it then gradually changed to a pale-yellow tint. It was left saturated with sulphuretted hydrogen at 0°, still retaining its pale-yellow colour. After an hour, it was freed from sulphuretted hydrogen by means of a current of hydrogen, the colour being observed to gradually deepen till it had the full yellow tint of indium sulphide. After 2¼ hours, only a very faint reaction for sulphuretted hydrogen was obtained.

$BaSO_4$ found.	Calculated for In_2S_3.
0·9575 gram.	0·9760 gram.

The decomposition has thus not only broken down the hydrosulphide, but is attacking the In_2S_3 itself. The interest of this experiment lies in the formation of the white compound from the hydrate; this is very probably the normal hydrosulphide, and the experiment suggests that in other cases where sulphuretted hydrogen acts on a metallic hydrate, it is not the sulphide, but the hydrosulphide, which is first formed. Thus, with copper, we do not have the sulphate formed and then taking up the sulphuretted hydrogen, but we have the hydrosulphide first formed and then breaking down. In the case of silver, on the other hand, the *sulphide* Ag_2S appears to be formed by the action of sulphuretted hydrogen on the hydrate, but in this case the action proceeds no further.

The same white indium compound, as is well known, is formed by treating indium sulphide with ammonium hydrosulphide.

Gold.

Our experiments on gold hydrosulphide were, unfortunately, made while we were unacquainted with the thorough work of Ludwig Hoffmann and Gerhardt Krüss on the sulphides of gold. As we assumed the formation of the trisulphide, Au_2S_3, this deprives our results of any quantitative value. There is, however, little doubt that gold sulphide has the power of combining with sulphuretted hydrogen, for, on drying the precipitated sulphide at 100°, distinct evidence of the evolution of the gas is obtained.

Our sulphides were obtained by allowing the gold solution to flow into sulphuretted hydrogen water kept continually saturated by a current of the gas. Under these circumstances, and in absence of excess of acid, a deep-brown *solution* of gold sulphide is obtained, which precipitates either on standing for some hours or on treatment with acid.

The following experiment, which we have not yet been able to repeat, was performed with a precipitate thus obtained. The sulphide was carefully extracted with carbon bisulphide. In washing the precipitate, a mixture of alcohol and amyl alcohol was used; a solution of carbon bisulphide in the mixture acts as a rapid solvent of sulphur.

$BaSO_4$ found.	Calculated for Au_2S_3.	Calculated for Au_2S_2.
1·1200 grams.	1·2190 grams.	0·8126 gram.

It is quite possible that we may here be dealing with a mixture of sulphides. This must be determined by further investigation.

SUMMARY.

Though as yet incomplete, the following points seem already proved by the above research:—

1. Of the metals precipitable by sulphuretted hydrogen almost all are capable of forming hydrosulphides.

2. These hydrosulphides are in some cases definite compounds of considerable stability, though of high molecular weight.

3. The action of acids seems, as a rule, to be to cause these hydrosulphides to lose part of their sulphuretted hydrogen and thus to produce compounds of higher and higher molecular weight.

4. That by dissolving the precipitated sulphates in sulphuretted hydrogen water, or other means, solutions of these hydrosulphides may be obtained, which sometimes exhibit no tendency to deposit a precipitate even after months of keeping.

5. The experiments tend also to support the conclusions that the sulphides themselves are in most cases polymerides of a very high molecular weight.

6. Among others, hydrosulphides, the composition of which agrees more or less exactly with the following formulæ, have been obtained:—

Copper	$7CuS,H_2S$; $9CuS,H_2S$; $22CuS,H_2S$.
Mercury ...	$31HgS,H_2S$; $62HgS,H_2S$.

7. Bismuth appears to be incapable of forming a hydrosulphide.

University College,
London.

X.—*The Physical Constitution of some Sulphide Solutions.*

By Harold Picton.

The difficulty of ensuring the complete precipitation of certain "insoluble" metallic sulphides has long been known. There has, however, been little or no systematic examination of the solutions of "insoluble" sulphides. In the previous paper, it has been shown that such sulphide solutions, of not inconsiderable strength, may be very easily obtained. I may here briefly recapitulate the methods employed :—

1. The metallic solution is allowed to run into sulphuretted hydrogen water kept saturated by a stream of the gas. It may then be freed from uncombined sulphuretted hydrogen by a current of hydrogen, or dialysed to free it from salts.

2. The metallic hydrates are suspended in water and treated with sulphuretted hydrogen.

3. The metallic sulphides, in a freshly precipitated state, are suspended in water and treated with sulphuretted hydrogen.

These methods are used according as, in the particular case, one or other is most applicable. The solutions obtained have been shown in the previous paper to contain combined sulphuretted hydrogen, to be, in fact, solutions of hydrosulphides.

By the first method we may obtain the solution of any metallic sulphide provided no great excess of acid be present. The second method is not always applicable, but has been used by us in the case of copper and zinc. The third method is applicable to mercury or copper. To give a general idea of the strength of these solutions, the following facts may be mentioned. An arsenide acidified with hydrochloric acid, if allowed to run into sulphuretted hydrogen water, will readily give a solution containing about 5 grams of sulphide in the litre, whilst in the case of mercuric sulphide, a solution containing about 10 grams of sulphide to the litre is readily obtainable. The question naturally suggests itself, Are these apparent solutions actually solutions, or do they merely contain the solid in a very fine state of suspension? When fairly dilute and free from salts, some of the sulphides show no symptoms of settling, even after several months. But the addition of salts or acid will often ensure rapid precipitation. On the other hand, the re-solubility of some of the sulphides after precipitation closely simulates true solution; for instance, on treating mercuric sulphide with sulphuretted hydrogen water, the sulphide redissolves. It is, at first sight, difficult to believe that the sulphuretted hydrogen should have power to cause very fine and suspension of the sulphide, but be unable to produce olution.

ons like these made it seem advisable to undertake a thorough investigation into the physical character of these solutions, which promised results of no little interest.

The solutions chosen for examination were those of mercury, arsenic, and antimony sulphides.

In general terms, the results obtained are as follows :—In the three cases under examination, the fact has been established that they are composed entirely of very minute, solid particles or of very large molecular aggregates. In all cases the particles are large enough to give results with Tyndall's experiment with a beam of light. They are, however, small enough in some cases to simulate the phenomena of liquid diffusion (in the absence of any membrane). They afford a series proceeding from what is more easily proved to be pseudo-solution to matter in a state which more strikingly simulates that of true solution. At one end of the series, we have pseudo-solutions, resolvable under a high power of the microscope into crowds of minute suspended particles in rapid Brownian movement; at the other end, we have solutions which refuse to be analysed by the microscope, which diffuse more or less after the fashion of true solutions, but which, even in exceedingly dilute solutions, reveal the presence of particles not too minute to scatter a beam of light.

These being, broadly, the results obtained, I will now proceed to give the experimental evidence, arranging it in such a way as to pass from more obvious pseudo-solution to what is more nearly allied to true solution as we are accustomed to conceive of it.

Mercury.

Preparation.—The sulphide precipitate may be prepared either in the ordinary way or by allowing an acidified solution of mercuric chloride to flow into sulphuretted hydrogen water. The carefully-washed precipitate is then washed into a Drechsel's bottle provided with stopcocks to prevent access of air, and there treated with sulphuretted hydrogen. In from one to two hours, the sulphide will have completely dissolved. The dissolved sulphuretted hydrogen may then be expelled by a current of pure hydrogen.

General Properties.—Solutions containing about 10 grams of sulphide to the litre may be readily obtained *free from uncombined sulphuretted hydrogen.* Stronger solutions are obtainable in presence of dissolved sulphuretted hydrogen. By transmitted light, the solution has a very clear, brown colour, which in strong solutions becomes so dark as only to be transparent in thin layers. By reflected light, the solution appears darker and somewhat turbid. When kept in absence of dissolved sulphuretted hydrogen, the upper part of the liquid in the course of five or six days becomes somewhat paler. The lower portions of the liquid grow denser and darker, and after some weeks the whole of the sulphide is slowly deposited as a precipitate. But though, as a final result, we have a precipitate formed, this is no adequate proof that in the freshly prepared solution we are not dealing with a true solution. In presence of sulphuretted hydrogen, the conditions are different; the behaviour of the sulphide under these circumstances is being investigated.

On the addition of salts, the sulphide is more or less rapidly precipitated.

Application of Raoult's Method.—It was thought that if there were true solution, some light might be thrown upon the molecular complexity of the dissolved hydrosulphide by the application of Raoult's method for determining molecular weights. No depression of the freezing point could, however, be detected, and, after freezing, a considerable quantity of the dissolved hydrosulphide remained precipitated. It is obvious that the failure to observe any depression might simply be due to very high molecular weight.

Microscopical Examination.—The most direct evidence on the subject would obviously be that of rendering the suspended particles, if such there be, visible to the eye. The first trials were made with a microscope having a magnifying power of about 600 diameters. From the result, I was at first led to suspect that a true solution was being dealt with. The clear field was not in any way resolvable. It seemed perfectly homogeneous. Owing, however, to some circumstances which once more suggested that the sulphides did not, in the ordinary sense, form perfect solutions, I decided to repeat the microscopical examination, using a higher magnifying power. A microscope, with an immersion lens and capable of magnifying about 1000 diameters, was kindly lent me by Professor E. A. Schäfer. The mercury solution was first examined with a power of about 800 diameters, the lens being immersed in the liquid. Sulphuretted hydrogen was in this case absent. The following is a description of what is seen. At first it is impossible to make out anything beyond a dimly granular appearance; but gradually one becomes aware of exceedingly minute particles in very rapid Brownian movement. The apparently homogeneous solution is really the scene of ceaseless oscillations of innumerable solid particles, crowded together so closely that very little free path is left. Indeed, this last fact is the probable explanation of their being seen at all. In a dilute solution, the motion most likely becomes so rapid as to render the particles invisible.

The presence of minute, vibrating particles in this apparently homogeneous solution is thus placed beyond dispute, but it is still quite conceivable that these particles are suspended in a certain amount of true solution. Other methods for ascertaining whether or not any true solution is present suggested themselves, but were not readily applicable to the case of mercury. Thus, for example, the diffusibility of the solution could not well be tried, owing to the fact that the mercury solution does not keep well in absence of sulphuretted hydrogen. These methods will be described under arsenic and antimony. Meanwhile, the result of two other experiments on the mercury solution may be mentioned.

Filtration through a Porous Cell.—A small porous cell was carefully washed till all traces of impurity had been got rid of. After closing the mouth of the cell by a caoutchouc cork, it was partially immersed in a mercuric sulphide solution and a vacuum created within the cell by means of a filter-pump. The liquid slowly filtered through, but was quite colourless, the sulphide being completely removed.

Spectroscopical Examination.—Observed in thin layers, the solution gave a continuous absorption in the violet and blue, no bands being observable.

Arsenic (α) *and* (β).

In the case of arsenic, it will be well to divide the subject into two sections, one of which will be discussed before, and the other after, antimony. Under the present heading, Arsenic (α), I shall set down the results obtained with two different arsenic solutions. One solution was obtained by dissolving arsenious acid in a solution of hydrogen potassium tartrate; the other was obtained from an acidified arsenite. When required free from salts, these solutions were subjected to dialysis.

α.—*Arsenical Tartrate Solution.*

Preparation.—Arsenious acid was dissolved by boiling with acid potassium tartrate. The solution thus obtained was diluted and allowed to run into sulphuretted hydrogen water. The liquid was then freed from uncombined sulphuretted hydrogen by a current of hydrogen.

General Properties.—Solutions containing about 5 grams of sulphide to the litre can be obtained; these, by transmitted light, have a clear yellow colour, becoming darker and slightly reddish in a strong solution. The solutions are strongly fluorescent, and by reflected light, look pale and turbid.

Weak solutions keep well, but the stronger ones deposit a small amount of precipitate after some months. The presence of sulphuretted hydrogen does not seem to affect this slight precipitation.

The solution may be boiled without producing precipitation. On long-continued boiling, however, the sulphide seems to be partially decomposed, though the solution is not precipitated (see previous paper).

Microscopical Examination.—In the case of this arsenic solution, it was more difficult to discern the presence of particles than with mercury. The full power of 1000 diameters was barely sufficient to resolve the solution into its constituent particles; these were exceedingly minute, but even with this power, it needed practice to discern them. A granular appearance could gradually be made out, and it then became apparent that the granules were endowed with a rapid dancing motion.

Diffusion Experiment.—No exact diffusion experiment was made in this case, but it was observed that the tartrate had the power of carrying out the arsenic particles by its own diffusion. The diffusion of the tartrate being due to its molecular motion, the bombardment of these molecules must have sufficed to move the sulphide particles.

Spectroscopical Examination.—The solution gave a continuous absorption in the violet and blue.

β.—*Solution obtained from an Acidified Arsenite.*

Preparation.—Arsenious acid was dissolved in caustic soda, and the solution allowed to flow into sulphuretted hydrogen water. The solution was dialysed to free it from salts.

General Properties.—In general appearance, &c., this solution is similar to that just described. A solution containing 5 grams of sulphide to the litre can readily be obtained. The solution, freed from salts, keeps distinctly better than the one described above; a bottle in my possession, closed with an ordinary stopper and thus somewhat liable to oxidation, has been kept for a year; it has deposited some precipitate, but the amount is small, and when last examined, the solution *still remained unresolvable by the microscope.* Salts, as usual, cause precipitation.

Microscopical Examination.—It has at present proved impossible to resolve this solution with the microscope. It presents the appearance of a perfectly homogeneous liquid.

Diffusion Experiments.—The diffusion experiments gave interesting results. The diffusion method is obviously of great use in determining whether the solutions are composed only in part or wholly of suspended solid. It was quite conceivable that the particles discerned in certain cases with the microscope only formed part of the whole sulphide present, and that the rest was actually in true solution. To attack this question, the following consideration was made use of. It was thought possible that whilst a true solution would be undoubtedly diffusible, suspended particles might very likely not diffuse. In the event of there being no diffusion, it was obviously proved that the *whole* of the sulphide present was in a state of suspension.

Graham's method for liquid diffusion was adopted, the liquid being placed in a small wide-mouthed bottle within a large beaker and covered with water. A solution of arsenic hydrosulphide, obtained by allowing an arsenite acid with hydrochloric acid to run into sulphuretted hydrogen water, was dialysed until free from all chlorides and sulphuretted hydrogen. It remained quite clear by transmitted light. The small bottle was filled with this solution, and closed with a glass plate attached to a glass rod. Water was then poured into the beaker, and siphoned out to remove traces of sulphide which had escaped in closing the bottle. Finally, the beaker was well filled above the level of the small bottle, and the glass plate carefully removed. After 32 days, there was absolutely no sign of diffusion; the outer water remained perfectly colourless, and contained no trace of arsenic. It is evident from this experiment that the *whole* of the sulphide is present in a state of suspension. No tendency to settle was exhibited by the suspended solid. It is noteworthy that these minute solid particles, though in rapid vibratory motion, are incapable of diffusion, and it is difficult to say exactly why they should not diffuse. It might be expected that a particle at the surface, finding its movement less hindered in one direction than the other, would pass beyond the general surface of the other particles. Yet this is not the case.

Antimony.

The only antimony solution obtainable is that resulting from the action of sulphuretted hydrogen on a solution of tartar emetic.

Preparation.—A moderately dilute solution of tartar emetic is allowed to flow into saturated sulphuretted hydrogen water.

General Properties.—The solution has a fine orange-red colour by transmitted light, and is only slightly fluorescent. It keeps well, but has a tendency to deposit small quantities of sulphide. The sulphide is not precipitated by boiling.

Microscopical Examination.—In this case again, it was impossible to ascertain the presence of particles by microscopical examination. The liquid appeared absolutely clear and homogeneous. Some of the tartrate solution was set dialysing on December 1, 1890. As the dialysis proceeded the solution was observed to become more strongly fluorescent. Renewed treatment of a portion of the liquid with sulphuretted hydrogen did not in any way diminish this fluorescence. On December 11, some of the liquid was examined microscopically, and it was now possible to discern the presence of excessively minute particles of about the same dimensions as those observable with the arsenical tartrate solution. On further dialysis, by which means all the tartrate present was eliminated, the antimony began to precipitate, and in the course of a few weeks was completely thrown down. This is interesting, as showing the progress of a gradual condensation occurring among the minute particles. There was no sudden or irregular change, but, apparently, a regular increase of size among all the particles, forcibly reminding us of molecular condensation. In what way the tartrate prevents this condensation, it is difficult to say.

Diffusion Experiment.—The method of diffusion was again used successfully to answer the question as to how this solution is constituted. But, as in this case the antimony solution cannot be obtained in absence of tartrate, it was necessary to use the device of having the same strength of tartrate both within and without the diffusing bottle. This was accordingly done. Some of the antimony solution was allowed to diffuse into tartrate of the same strength from June 5 to June 29. During this time no diffusion occurred. This settles the question as regards the antimony solution, and proves that it is not a true solution. Subsequently it was thought that perhaps the particles might be smaller and more capable of diffusion when much diluted. A very dilute antimony solution was set diffusing on July 27, 1891. By October, absolutely no diffusion had occurred; indeed the liquid had settled somewhat in the bottle, owing perhaps to the dilution of the acid tartrate present.

When the outer liquid does not contain tartrate, diffusion is at once observed.

Tyndall's Experiment.—Tyndall has shown that light, scattered by finely-divided particles, is completely polarised.

Some of the antimony solution was sealed in a tube, and a beam of light from a lime-light lantern passed through the liquid. The rounded extremity of the tube acts as a concentrating lens, and enables the path of any beam to be very clearly traced. In this case, the track of the beam was marked by a beautiful, soft, red glow, the light of which, on examination with a Nicol's prism, was found to be completely polarised. The solution, therefore, has no true fluorescence, but consists of excessively minute particles in suspension. The most dilute antimony solutions gave similar results.* The distilled water employed showed practically no beam.

Filtration through a Porous Cell.—A porous cell was kept exhausted by a filter-pump and plunged into the freshly-prepared clear, red antimony solution. The liquid filtered through was quite colourless. This experiment tends to support the belief that the whole of the antimony is present in suspension.

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* Applied to the mercury sulphide solution above discussed, this experiment, as might be expected, yields similar results.

Coagulation Experiment.—As another means of testing the condition of the dissolved sulphide, that of its sudden coagulation was used. A true solution so coagulated should develop heat. Careful experiments were made on coagulating a strong antimony solution with a few drops of calcium chloride. Not the smallest change of temperature could be observed, although a change of 0·02° could have been easily seen with the thermometer used.

Spectroscopical Examination.—Like all the other sulphide solutions examined, this liquid gave a continuous absorption in the violet and blue.

Arsenic (γ).

In this case, the solutions were obtained from pure arsenious acid dissolved in water. The acid was dissolved by continuous boiling, and, under these conditions, a strong solution may be obtained.

Preparation.—The arsenious acid was allowed to flow into saturated sulphuretted hydrogen water, through which a current of the gas was continually passing. The uncombined sulphuretted hydrogen was then removed by a current of hydrogen.

General Properties.—In appearance this solution resembles arsenic (α) and (β). It readily forms solutions containing 11 or 12 grams of sulphide to the litre. A strong solution kept for four months in a sealed bulb has deposited a mere trace of precipitate. Weak solutions, kept for the same time, are almost entirely unchanged. But the permanence of the solution is somewhat variable. Though clear by transmitted light, the strong solutions have by reflected light a densely milky appearance.

The solution is not precipitated by boiling, but the addition of certain salts rapidly effects precipitation. Calcium chloride is here again specially potent.

Microscopical Examination.—The microscope, as might be expected from the case of arsenic (β), affords no evidence of the existence of solid particles.

Diffusion Experiments.—On account of the results invariably obtained in other cases, it seemed hardly worth while to submit this solution to the diffusion test. However, I decided to perform the experiment. The same apparatus was used as in the case of arsenic (β). To my surprise, by the following day, distinct diffusion was observed. It seemed just possible that the diffusion might be due to some impurity. Another specimen of resublimed arsenious oxide was therefore used, and, after treatment with sulphuretted hydrogen, was very carefully freed from uncombined gas by a current of hydrogen. This specimen, however, again diffused markedly in the course of a few days.

It occurred to me that perhaps some small quantity of true solution might be at first formed which would disappear on keeping. To give time for further condensation, some of the sulphide solution prepared as above described was accordingly sealed up in a glass bulb at the end of July. On October 14, the bulb was opened and some of the liquid placed in the small diffusion bottle. This was then closed with a glass plate in the usual way, covered with distilled water, and left covered till next day to acquire the temperature of the room. On October 15, the diffusion bottle was uncovered at 1 o'clock, the outer liquid being left quite colourless. By the next day, marked diffusion had occurred, which day by day increased. It had been previously observed that on prolonged diffusion with exposure to air, the sulphide solution becomes altered, arsenious acid being found in the outer liquid. In the present case, therefore, the diffusion was stopped on October 26, by which time the outer liquid was deeply coloured. The diffusion is of course slow, but to give some rough idea of its rate the following numbers are given. The diffusion in this case occupied 11 days. The main object of the experiment was to ascertain whether a weighable quantity would diffuse.

Capacity of small bottle.	As_2S_3 in bottle.	Volume of outer liquid.	As_2S_3 in outer liquid.	Diameter of bottle.
77 c.c.	0·8210 gram.	350 c.c.	0·1185 gram.	30 mm.

The diffusion of a dichromate solution of similar strength would be completed in five or six days.

We have here the rather remarkable fact of particles so small as to diffuse after the fashion of the molecules of a liquid, yet revealing themselves as solid particles under the scrutiny of other tests. That the diffusion is due to the motion of the particles themselves, and not to that of the water molecules, is made quite clear from the previous diffusion experiments. For instance, with antimony it was found that diffusible substance (acid potassium tartrate) could carry out the sulphide when present in the little bottle alone, but not when present in equal strength throughout both liquids.

Tyndall's Experiment.—On sending a beam of lime-light through the diffusible arsenic solution, the track of the beam was marked by a soft, yellow glow, the light of which, when examined by a Nicol's prism, was found to be completely polarised. This is proof positive of the existence of solid particles, but how is the presence of any true solution to be disproved? Analogy forcibly suggests that this solution will resemble the others in being homogeneous rather than partly solution and partly suspended solid. But something more than this is needed.

Obviously, if there be any true solution, it is this which will be *first* formed on allowing the arsenious acid to flow slowly into sulphuretted hydrogen water. Hence, if a very dilute solution be thus carefully prepared, there should be no particles present capable of revealing themselves in a beam of light. Accordingly, some dilute arsenious acid solution was allowed to flow very slowly into sulphuretted hydrogen water. An exceedingly dilute sulphide solution of a faint yellow colour was thus obtained.* When examined with a beam, the track of the light was, however, still marked by a soft glow of polarised light. This seems to leave little room for doubt that the diffusible sulphide solution is entirely composed of particles sufficiently large to scatter light. The fact that after long keeping the sulphide still retains its diffusibility also forcibly suggests that the diffusibility is not due to the presence of a little true solution at first formed. It is inconceivable that a solution so unstable as to be partially precipitated even in exceedingly dilute solutions when first formed could remain unchanged for months in the presence of a comparatively vast amount of solid.

Coagulation Experiment.—It was thought that perhaps some evidence as to the state of the sulphide might be obtained from sudden coagulation of the liquid. Careful experiments were made by coagulation with a few drops of calcium chloride, but not the slightest change of temperature was discernible.

Application of Raoult's Method.—No perceptible depression of the freezing point was obtained.

Some General Properties of the Sulphide Solutions.

It has already been observed that these solutions are precipitated by salts or acids. But these bodies are by no means equally active in producing precipitation. The following substances were added to an arsenic solution [arsenic (β)] with the results stated.

Precipitate (but sometimes only when strong).	Do not precipitate.
Calcium chloride (at once).	Sodium borate.
Sodium chloride.	Sodium acetate.
Ammonium chloride	Ammonium succinate.
Chrome alum.	Gallic acid.
Sodium phosphomolybdate.	Alcohol.
Sodium phosphate.	

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* These dilute arsenious sulphide solutions are beautifully clear and transparent, and by their appearance suggest that they are perfect solutions.

On freezing the solutions completely, almost the whole of the sulphide is precipitated. The similarity of the absorption spectra has been already noted.

On evaporation in a vacuum, mercury and arsenic sulphides yield a colloidal mass.

Summary.

The sulphide solutions examined have been shown to consist entirely of very minute solid particles in each case revealed by Tyndall's experiment.

In two cases, mercury and arsenic (α), these particles have been found to be visible with a powerful microscope, and have been observed to be, as nearly as could be determined, of the same size and all in rapid vibratory motion. In one case, that of antimony, the gradual condensation of the particles from those quite invisible under the microscope to those just visible, but of uniform size, and finally to larger aggregations ultimately settling as precipitate, has been followed.

In the case of arsenic (γ), these particles are so finely divided, or vibrate so rapidly as to simulate the behaviour of molecules composing a liquid. They are capable of diffusion, and retain this power even after prolonged keeping.

The obvious theoretical suggestions of these experiments I propose to deal with in the next paper, in which a number of observations on colloid solutions will be recorded. In closing, however, it may be pointed out that while sulphuretted hydrogen can split up mercuric sulphide into minute vibrated particles in a state of very perfect suspension, and arsenic sulphide is capable of existing in a state of suspension so perfect as to simulate the phenomena of liquid diffusion, but yet revealing solid particles by Tyndall's experiment, it is easy to conceive of a case in which the process of subdivision has gone still further, and Tyndall's experiment is no longer adequate to discover the suspended particles. Passing on from this, there seems no satisfactory reason for imagining the existence of any sharp boundary between solution and pseudo-solution. It is quite possible that the one merges by imperceptible gradations into the other. In this event, the vibratory motion of these minute particles, which so forcibly reminds one of molecular motion, becomes a phenomenon of special interest. This subject will be more conveniently dealt with in the following paper.

University College,
London.

XI.—*Solution and Pseudo-solution.* Part I.

By HAROLD PICTON and S. ERNEST LINDER.

INTRODUCTION.

IN the previous paper, one of us has examined three special cases of apparent solution, namely, those of mercury, antimony, and arsenic sulphides. These liquids, which in many ways resemble ordinary colloidal solutions, were found to present a series passing from matter in a state of subdivision not too fine to allow of its observation under the microscope, to particles so fine as to diffuse in the manner of ordinary solutions. Arsenic sulphide, indeed, was found capable in itself of presenting us with three different types of solution, distinguished in the paper as arsenious sulphide α, β, and γ. Arsenic α is made up of particles just visible under the microscope, arsenic β contains no visible particles, whilst arsenic γ contains particles so minute as to be diffusible. The case of mercury sulphide was specially interesting, as the sulphide, after precipitation, is easily dissolved in sulphuretted hydrogen water, and in this solution the vibrating particles are clearly discernible under the microscope (see previous paper).

We have here what appears to be a half-way stage towards true solution. The suggestion is at once forced upon our minds that the state of pseudo-solution would gradually merge into that of true solution by carrying the subdivision farther and farther, till finally, perhaps, we may have the substance dissociated into ions. To trace the steps somewhat further would obviously be a task of no little interest. And on asking ourselves what solutions are most likely to furnish stages in the phenomena of solution between those of arsenic γ and those of true solution, the case of ordinary colloidal solutions at once suggests itself. Thus the investigation into the nature of the sulphide solutions just described had not proceeded far before it was determined to follow it up with some experiments on a variety of colloïdal solutions. Some of these have now been examined, and we have also obtained interesting evidence with regard to the transition from colloidal to crystalloidal solution, part of which we shall lay before the Society in this paper.

Before describing our own experiments, it will be well to give a short account of previous work on the subject.

Graham, it will be remembered, supposed the non-dialysability of colloids to be due to the size of their molecules, which he considered too large to pass through the pores of the membrane. A certain mystery has long hung about the facts of colloidal solution, and that colloids are substances of very great molecular complexity has of late become increasingly evident. Theory has oscillated between the two conceptions of very large molecular aggregates and very finely divided particles. Perhaps in the end the two theories mean the same thing.

Ostwald (*Lehrb. d. allg. Chem.*, **1**, 52) and Paternò (*Zeit. physikal. Chem.*, **4**, 457) have both suggested that colloidal solutions are probably composed of very finely divided solids in a state of suspension. But experimental evidence has been almost entirely wanting.

Barus and Schneider, in a paper on colloidal silver in the *Zeitschrift für physikalische Chemie* (**8**, 278), have recently made an attempt to supply this want. They support the theory that colloidal solution in general is merely a condition of suspension.* With the main tendency of their arguments we are in agreement, but there are some portions of their work to which we are obliged to take exception. We propose to briefly examine the paper here. Barus and Schneider have specially investigated the case of Carey Lea's soluble silver. Their solutions were obtained by reducing with ferrous citrate, and redissolving the silver thus obtained. The solution presents many points of similarity to the sulphide solutions discussed by one of us in the previous paper. It is slightly fluorescent, it is coagulated by the addition of certain substances, and also by freezing, but it does not settle spontaneously. The solution, however, does not lend itself so easily to exact chemical or physical examination, since it cannot be obtained free from iron salts.

The experimental work of the paper may be considered under two heads: first, experiments on the electrical resistance of the silver solution; and, secondly, experiments on the sedimentation of the solution when partially coagulated. The silver in solution is found to act as a non-conductor; indeed, according to the experiments, the stronger the silver solution the greater the resistance. This is somewhat unintelligible, but the measurements are complicated by the presence of electrolytes in the solution. From the fact that the metallic silver in solution does not act as a conductor, they conclude that it is not present in the molecular state, but rather in the condition of finely-divided suspended particles. This reasoning appears, however, to us to be by no means conclusive, for what evidence is there that would lead us to expect silver in a state of true solution to act as a conductor?

The coagulation of pseudo-solutions, on the addition of certain salts or acids, cannot be ascribed merely to diminished viscosity of the water, since the traces of acid or salt necessary would be quite inadequate to produce so profound an effect. This had previously been shown by Barus. The authors suppose the coagulation to be due to the separation of the particles.

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* To prevent any misconception, we may say that our work on the sulphides (see preceding papers) was begun in 1888, and that the present paper was actually being prepared before we became aware of this work.

To arrive at some idea of the size of the silver particles, the authors make use of the following equation :—

$$x = \frac{2}{9\eta} r^2(\rho - \rho')g,$$

where x = rate of subsidence of the particle.
η = viscosity of the suspending medium.
ρ = specific gravity of particle.
ρ' = specific gravity of medium.
r = radius of particle.

Now x, η, ρ, and ρ' are constants, g is obviously constant, and thus r alone varies.

As the silver particles do not subside, they have to base any calculations on a partially coagulated solution. Inserting values in the above equation, and taking Kohlrausch's value for the size of the water molecule, they find that the diameter of the particles in a *coagulating* silver solution may be as small as that of 70 water molecules. Calculations of this kind are very fascinating, but we confess to grave doubts as to the validity of the above equation. It is evident from the fact that the solvent can effect this fine subdivision, that there is some action between solid and solvent, whilst the above equation presupposes none. The fact, too, that particles visible under the microscope exhibit so very little tendency to settle does not seem to coincide with the assumptions of the equation.*

Prange is quoted as having observed evolution of heat on coagulation of the silver solution. Prange is also quoted as having obtained a negative result with Tyndall's experiment (*Rec. d. Trav. Chim. des Pays-bas*, **9**, 125).

The evidence upon which most stress is laid in the above-quoted paper seems to us to be decidedly inconclusive. It is also noteworthy that throughout this paper there is an assumption that if the colloidal solutions contain very finely divided particles, the solution is a fact of *mere* mechanical suspension and nothing more. This is evident, too, from their method of calculating the size of the suspended particles. An assumption of this kind seems to us to be quite irreconcilable with fact. There is a reaction *other than mechanical* between the solvent and the solid, even in these cases of colloidal solution. Otherwise the re-solubility of precipitated colloids becomes an impossibility, and the extreme permanence of some colloidal solutions is exceedingly hard to explain. Moreover it will be shown, in at least one case in the following paper, that there is undoubted molecular attraction or chemical combination between the colloid and its solvent.

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* Compare some observations of Jackson (*Proc. Chem. Soc.*, 1891, 178) mentioned in the discussion of this paper.

General Statement.

Our intention in this part of the paper is to carry further the examination, begun by one of us, into the connection between suspension and solution. We have now made a general survey of the ground, and we propose in this section to trace further the change from obvious suspension to true colloidal solution, and to make some attempt to follow the apparently continuous change into the regions of crystalloidal solution. Our object being to follow this continuous change, rather than to examine individual cases, we have embodied in the present part results obtained with typical examples, and we shall leave the examination of a larger array of individual cases for a future occasion.

Whatever can throw any light upon the *mechanism* of solution must be of interest. We have undertaken to follow up the various states of suspension and solution through their different grades, in the hope that an exact examination of the changes which occur in the passage from one grade to another may shed some light upon the vexed question, What is it that happens when a body dissolves?

The questions to which we seek an answer in these researches are, broadly, the following:—

What is the nature of colloidal solution? Does the solid, dissolved in these solutions, exist in the form of finely-divided particles, discernible by optical or other means? If such be the constitution of any colloidal solution, would it in any case be possible to see these particles under the microscope? Does the dissolved substance in any crystalloidal solution exist in the form of particles which can, by any means, be discerned? May there be a perfectly continuous gradation from suspension to crystalloidal solution? Supposing that such a series can be made out, what is the nature of the forces by which, in the lower grades of solution, the particles are held in suspension? What is the nature of these finely-divided particles, if they exist?

In the following pages we hope to show how these questions can be answered.

Experimental Results.

The colloids at present examined have confirmed the suspicions suggested by the investigation of the sulphide solutions. The present paper only deals with the few cases at present examined, and does not pretend to be in any way exhaustive. The results of the more extended investigation which we intend to undertake, both of colloidal solution, and, if possible, of its passage into crystalloidal solution, we shall embody in Part II of this paper, which we hope to be able before long to lay before the Society. In the present part, we shall set down briefly the results obtained with the solutions already examined. Of inorganic colloids, the following have been examined:—

Ferric Hydrate.

The hydrate was precipitated with ammonia from a solution of ferric chloride, well washed, and then placed in a solution of ferric chloride, in which it soon dissolved. Without dialysing out the excess of ferric chloride, some of this was examined, whilst another portion was dialysed till the outer water contained no trace of chloride.

The solution was, in both cases, fluorescent, but absolutely clear by transmitted light.

Microscopical Examination.—A magnifying power of 1000 diameters was found quite inadequate to reveal any want of homogeneity in the structure of the solution.

Tyndall's Experiment.—A tube of the undialysed liquid was sealed and examined with a beam of light, in the same manner as the sulphide solutions (see p. 143). A dense glow was observed in the track of the beam, the light of which was completely polarised. To confirm this result, a portion of the liquid which had been examined was treated with hydrochloric acid till the hydrate was entirely dissolved. The track of light was no longer visible, with the exception of the very feeble beam always observed, even with distilled water. The dialysed solution showed the track of the beam so markedly that it was only necessary to hold the tube under an ordinary gas jet to observe the effect.

Filtration through a Porous Cell.—Ferric chloride solution having been saturated with the hydrate, the liquid was dialysed. The ferric chloride was evidently, for the most part, combined with the hydrate, for only slight diffusion was observed. Dialysis was continued till the outer liquid showed no trace of iron or of chloride. The dialysed liquid had, by transmitted light, a clear, deep, ruby-red colour. It was filtered, under pressure, through a porous cell. The filtrate contained no trace of either iron or chloride. Evidently, therefore, any remaining ferric chloride was held in combination by the hydrate. None of the compound is present in a sufficiently finely-divided state to pass through a porous cell.

Coagulation Experiment.—The solution is easily coagulable by calcium chloride. On coagulation, the *whole* of the iron passes out of solution, the filtered liquid containing no iron. The combined molecules of hydrate and chloride coagulate without dissociation. It is thus quite clear that, in this case, there is a chemical attraction between the molecules of the solvent (ferric chloride) and the solid (ferric hydrate).

The act of coagulation is not accompanied by any evolution of heat. The molecules, or particles, are too large to produce perceptible evolution of heat on condensation.

Diffusion Experiment.—Some of the dialysed hydrate was set diffusing, without a membrane, on a Saturday. By the following Monday no diffusion had occurred. This places the state of subdivision at a probably lower stage than that of the diffusible arsenic sulphide. But, on the other hand, the result might, perhaps, be due to slower rate of vibration without increase of size.

Crystallisability of the Solution.—It is stated that a strong solution of ferric hydrate in ferric chloride, when evaporated in a vacuum, deposits crystalline plates of the compound $9Fe_2O_3,FeCl_3$.* If this be so, we have the remarkable fact of crystallisation in a body, the molecular aggregates of which are sufficiently large to scatter light, as shown by Tyndall's experiment. The proportion of chloride present, according to this formula, being, probably, larger than that in our solution, a considerable excess of ferric chloride was added to some of the colloidal hydrate, with a view to determine any change in the character of the solution. Immediately after the addition, it was examined with a beam of light. The same appearance was noticed as in the case of the original hydrate. After two or three days had elapsed, it was again examined. Just the same luminous beam was still observed.

Chromic Chloride.

While engaged in preparing some colloidal chromium hydrate, we had occasion to notice certain facts with regard to the solubility of chromium chloride. As is well known, prolonged boiling with water will only effect gradual dissolution of chromium chloride. The addition of a trace of chromous chloride, however, makes it dissolve much more rapidly. In our case, some beautifully crystalline "resublimed" chromic chloride was treated with water, and a little chromous acetate, containing excess of hydrogen chloride, then added. In the cold, dissolution was slowly effected. Some of the liquid was allowed to stand for some time, and then sealed in a glass tube.

* This formula is taken from Ramsay's *System of Inorganic Chemistry.*

Tyndall's Experiment.—The liquid was examined in the same way as before, and was found to give a well-marked, soft beam. We concluded that the chromic chloride was probably dusty or impure. After keeping it a few days, the tube was again examined, and this time the track of the beam of light was no longer visible. The hydrochloric acid present would prevent the formation of basic salts. From the results of our other experiments, it seems to us most probable that we are here actually observing the slow breaking up of molecular aggregates with the final formation of a crystallisable solution. The theoretical meaning of these experiments will be discussed further in the sequel.

Chromic Hydrate.

The solution of chromic hydrate in chromic chloride shows a well-marked, luminous beam. It was, therefore, needless to examine the dialysed solution. The chromic chloride used showed no luminous beam.

Aluminium Hydrate.

The solution of aluminium hydrate in the chloride showed a well-marked, luminous beam.

Both these solutions are thus similar to the ferric hydrate solution.

Silicic Acid.

Silicic acid affords a very characteristic case of colloïdal solution, and it is thus of obvious interest to examine it. Sodium silicate solution was treated rapidly with excess of hydrochloric acid so as to redissolve the silicic acid formed.

I. *Solution in Presence of Hydrochloric Acid.*

Tyndall's Experiment.—The undialysed solution, in presence of a very slight excess of hydrochloric acid, showed *no luminous beam* on passing a ray of light through the liquid. Some of the dialysed solution, to which hydrochloric acid had been added, showed no luminous beam. Some of the silicic acid solution, in presence of hydrochloric acid, was gelatinised by evaporation and redissolved in presence of acid. It showed no luminous beam. It is, therefore, evident that, in presence of hydrochloric acid, silicic acid does not in solution form molecular aggregates of sufficient size to scatter light.

Evaporation.—As the solution did not scatter light, it was thought that if evaporated in presence of hydrochloric acid it might possibly crystallise. Some of it was allowed to slowly evaporate in a current of dry air mixed with hydrochloric acid. It gelatinised, however, thus seeming to behave like a colloid, though too finely subdivided to yield a positive result with Tyndall's experiment.

Filtration through a Porous Cell.—A strong solution of silicic acid was obtained by the rapid addition of hydrochloric acid to sodium silicate. The solution was then filtered as before through a porous cell. Silicic acid at once came through in large quantities. It was obtained in the amorphous state after evaporation on the water-bath and dissolving out the sodium chloride. This result is particularly interesting as presenting us with the case of a colloid the molecules of which can pass through the fine pores of a cell. The cases of ferric hydrate and hæmoglobin are in interesting contrast to this.

II. *Dialysed Solution Free from Hydrochloric Acid.*

The solution was set dialysing on Wednesday. It was left, with frequent changes of water, till Saturday, and then without change till Monday. The solution was now free from chloride.

Tyndall's Experiment.—A portion of the solution was sealed up on Monday (October 19). Examined with lime light, it gave a very feebly luminous beam, scarcely greater than that observed with ordinary distilled water. On Tuesday, the tube was re-examined, and this time a distinct, soft glow was observed in the track of the light. Obviously, a slow condensation was taking place after the removal of the hydrochloric acid. From October 23 to November 23 no further change has been observed in the tube.* The silica, in presence of a very slight excess of acid (see above), continues to show no beam. A few filaments of silica have, however, developed in the tube. The other acid solutions (see above) are unchanged.

Molybdic Acid.

Some pure "colloidal molybdic acid" solution was kindly lent us by Miss Aston. The solution was allowed to stand in tubes for about 10 days, to allow some small, solid particles to settle. On evaporation on the water-bath, the solution leaves a gelatinous film which breaks up into radiating rods, giving it an almost crystalline appearance. Evaporated over sulphuric acid, a gelatinous residue is also obtained.

Tyndall's Experiment.—Only a very faint track of light, like that observable with distilled water, could be seen on passing a ray of light through this liquid. The solution does not, therefore, contain molecular aggregates large enough to possess the power of scattering light.

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* The silica solution was dilute.

Filtration through a Porous Cell.—The molybdic acid passes at once through our porous cell.

The following *organic* substances have been examined :—

Cellulose.

Cellulose was dissolved in Schweitzer's solution, and the clear liquid allowed to settle for several days. The Schweitzer's solution itself showed a very feeble luminous beam when a ray of light was passed through it.

Tyndall's Experiment.—The cellulose solution showed a well marked glow when the ray of light was passed through it. The light of this glow was, as usual, polarised.

Starch.

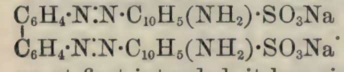
Soluble starch was prepared by dissolving starch in glycerine, pouring into water, and then precipitating by alcohol. The precipitated starch was redissolved in water and again precipitated. A strong solution was made from the starch so obtained.

Tyndall's Experiment.—A tube of the clear solution showed a well-marked, luminous beam with a ray of light. Polarisation was complete.

Diffusion Experiment.—A strong starch solution was set diffusing on Wednesday, July 8. By a siphon, fixed to the side of the beaker, samples of a diffusate could be drawn off without causing any disturbance in the liquid. On Wednesday, July 15, samples of the outer liquid were drawn off. This gave so faint a colour with iodine that, in a test-tube, the tint was hardly perceptible. Practically, no diffusion had occurred. It is no use exposing the starch solution to more prolonged diffusion, as it undergoes chemical changes, and the experiments are thus invalidated. Some of the starch solution from the diffusing bottle was tested with a ray of light, and gave a well-marked, polarised beam.

From these experiments, it appears probable that the starch exists in solution in states of aggregation larger than those of a diffusible arsenic solution.

"*Congo-Red.*"

In some experiments on the filterability of bodies of varying molecular complexity through porous pots, we made use of Congo-red,  $\begin{array}{l} C_6H_4{\cdot}N{:}N{\cdot}C_{10}H_5(NH_2){\cdot}SO_3Na \\ | \\ C_6H_4{\cdot}N{:}N{\cdot}C_{10}H_5(NH_2){\cdot}SO_3Na \end{array}$. Though not of service for the purposes we at first intended, it has yielded, among others :—

I. *Neutral Solution.*

Congo-red dissolves very easily in water, giving a deep, red-brown solution.

Tyndall's Experiment.—The fluorescent solution gives a well-marked, polarised beam.

Filtration through a Porous Cell.—The very deep-coloured solution was filtered under pressure for nearly two hours. *At least* 60 c.c. of water were passed through the small porous pot. The inner liquid showed only a faint tinge of colour, probably due to some slight leak.

Diffusion Experiment.—In this experiment, a slight amount of coloration of the outer water was noticed during the first two days, but did not afterwards perceptibly increase. The coloration might be due to slight currents or to the presence of some diffusible substance. Certainly the Congo-red, as a whole, did not diffuse. The same solution was recovered on Friday, the outer water changed, and the diffusion allowed to proceed till Monday. A very slight coloration of the outer liquid was observed, less than in the previous case.

II. *Acid Solution.*

The acid Congo-red has a fine purple-blue colour.

Tyndall's Experiment.—With a ray of light, this gives a well-marked, polarised beam.

III. *Alkaline Solution.*

The alkaline Congo-red has a clear, red colour without the brown tinge of the neutral substance.

Tyndall's Experiment.—This solution showed no luminous beam when a ray of light was passed through it.

Filtration through a Porous Cell.—Filtered under pressure, the filtrate was in 20 minutes as strongly coloured as the outer liquid.

Hæmoglobin.

In seeking for a body likely to be of service in connecting colloidal with crystalloidal solution, we naturally turned our attention to the case of hæmoglobin. This substance is easily obtained; it forms several readily crystallisable derivatives, and it affords an instance of enormous molecular complexity. Its percentage composition (dog) is given as:—C, 53·85; H, 7·32; N, 16·17; Fe, 0·42; S, 0·39; O, 21·84. Preyer assigns it the empirical formula $C_{600}H_{960}N_{154}FeS_3O_{179}$. It is possible that the molecular weight may be much greater than this.

Owing to the small percentage of iron present, this is the simplest formula that can be assigned. Obviously it is of great interest to determine the analogies between a crystallisable solution containing these exceedingly complex molecules and the colloidal solutions, some at least of which we have seen contain aggregates large enough to scatter and polarise light.

I. *Oxyhæmoglobin.*

Preparation.—Fresh, defibrinated dog's blood was shaken with ether and allowed to stand till it had formed a magma of crystals The liquid was then centrifugalised, the upper layer drawn off, and the crystals well stirred with water and alcohol. The mixture was again centrifugalised, the washing being repeated five times. The crystals thus purified from serum-albumin were dissolved in the smallest quantity of water, alcohol added, and the solution allowed to stand in ice. In the course of 24 hours, the hæmoglobin had again crystallised out. After once more centrifugalising, the hæmoglobin obtained was used in the following experiments. The red mass, when examined under the microscope, showed a beautifully crystalline structure.* On allowing some of these crystals to drop into water, they dissolve, especially if the water be very slightly warmed, forming a beautiful, clear, red solution.

Tyndall's Experiment.—Some of the red solution was filtered, a few floating particles being discernible. The perfectly clear liquid was then examined with a ray of lime light. A distinct, soft, luminous beam was observed, the light of which was completely polarised. The solution contained about 0·3 or 0·4 per cent. of oxyhæmoglobin, and it seems quite impossible that in a solution so dilute there could have been sufficient impurity to account for this beam. Besides this, presence of dust or other solid impurities is indicated by a beam of quite different appearance, and, if the expression may be permitted, by one far less close in texture. We have every reason to believe that the hæmoglobin solution thus carefully prepared contains no impurity sufficient to mar these results.

Examined spectroscopically, the solution gave the characteristic and well-marked absorption spectrum of oxyhæmoglobin.

We have here what is probably the second case (see ferric hydrate) of a crystallisable solution revealing the presence of molecular aggregates or molecules sufficiently large to scatter light.

Filtration through a Porous Cell.—This method seems to possess considerable advantages over the ordinary one of dialysis. In the first place, it is difficult to obtain a thin membrane quite free from inequalities, and, in the next place, the process of dialysis is, necessarily, rather prolonged, and in the case of rather unstable bodies is, therefore, not very applicable. The crystallised hæmoglobin is said to be capable of diffusing *very slowly* through animal membranes. Owing to the rapid and decisive results obtained by the above method in other cases, we applied this test to the dissolved hæmoglobin crystals. The solution was, therefore, filtered under pressure in the way described in the previous paper. After filtering for 2 or 3 hours and thus obtaining three cellfuls of filtrate, the liquid still came through the cell as clear and colourless as pure distilled water, while the outer liquid had a brilliant scarlet hue. The hæmoglobin molecules or their aggregates are, therefore, too large to pass through the pores of our porous cell. As in the case of other solutions possessing this property, the molecular aggregates are large enough to scatter and polarise light.

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* It is quite possible, with appropriate means, to obtain crystals several centimeters in length, but for our purpose the above method was sufficient. These crystals can be obtained from defibrinated blood without any addition of alcohol.

These results make it impossible to avoid the conclusion that there is no hard and fast line between colloidal and crystalloidal solution. More strikingly does this seem to be the case when we remember that silicic acid, in presence of hydrochloric acid, passes readily through the pores of a porous cell, though it has not been obtained crystalline from this solution, and must, therefore, at least crystallise far less readily than hæmoglobin.

II. *Carbonic Oxide Hæmoglobin.*

This derivative of hæmoglobin is crystalline and very stable. Stirling mentions that he has kept carbonic oxide hæmoglobin in a stoppered bottle for four years without alteration (Landois and Stirling, 1, 34). It is readily obtained by passing carbonic oxide through a solution of hæmoglobin. The solution thus obtained from the recrystallised hæmoglobin was examined spectroscopically, and showed the characteristic shifting of the two oxyhæmoglobin bands towards the violet.

Tyndall's Experiment.—Examined with a ray of light, the solution showed a well-defined, luminous beam. A strong solution of the carbonic oxide hæmoglobin was recrystallised, and some of the crystals redissolved. The same beam was again observed, and the light was found to be completely polarised.

Filtration through a Porous Cell.—As in the case of oxyhæmoglobin, the solution could not pass through the pores of the cell. The filtrate was absolutely colourless. It is noteworthy that this observation coincides with the general rule, hitherto observed, that nonfilterability is coincident with inability to scatter light. Exceptions to this rule may, however, be hereafter found.

Magdala-Red. Naphthylamidoazonaphthalene ($C_{30}H_{20}N_4$).

This substance, being readily obtainable, was chosen as a crystalline body of less complexity than hæmoglobin, but still possessing a complicated molecule. Its vivid colour also made it peculiarly serviceable in our experiments (see below). The solution in alcohol is bright pink by transmitted light, and has a magnificent golden fluorescence.

Tyndall's Experiment.—The track of the ray of light was marked by a beautiful glow of colour. When examined with the Nicol's prism, the scattered light was found *not* to be polarised.

Filtration through a Porous Cell.—The alcoholic solution filtered through a porous cell at once showed the vivid colour of Magdala-red in the filtrate.

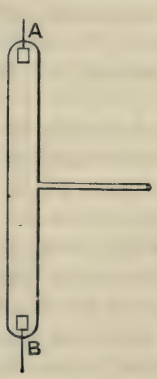
A new Property of certain Solutions.

We propose in this place to give some preliminary account of a remarkable property we have observed in some solutions; this consists in the repulsion of the dissolved substance as a whole from one pole to another when we immerse in the liquid electrodes connected with a galvanic battery. Our experiments are not, as yet, far advanced, but it seems appropriate in this place to give a preliminary account of them, as they may prove of service in ascertaining the connection between colloidal and crystalloidal solution. We do not propose to do more here than give some of the experimental results obtained. It is difficult to frame a theory which will account for them, but the facts are as follows. We will give, first, the results obtained with arsenic sulphide, as this substance was most thoroughly investigated; and then some experiments dealing with substances ranging from pseudo-solution to crystallisable solution.

Arsenious Sulphide.—The first experiments consisted in immersing the electrodes connected with a storage battery in some of the diffusible arsenic sulphide solution. As was expected, no appreciable electrolysis occurred, but the sulphide was gradually driven down below the electrodes. It showed no signs of coagulation, but, on the contrary, when the connections were broken, it began to diffuse up slowly through the liquid. This is not an effect of decomposition, nor does gravity play more than a subsidiary part, as is shown by the subsequent experiment.

In the next experiment, a V-tube was partially filled with the arsenic solution and the electrodes just immersed in the liquid. The electrodes were at a distance of about 30 cm. from each other. In about 10 minutes, the sulphide was observed to be descending from the negative electrode. The descent slowly continued till about 6 cm. of colourless liquid were observable at the negative pole. The liquid at the positive electrode was, meanwhile, unchanged, and remained so for an hour and a half, during which it was observed. The experiment was left all night, and by next morning a considerable descent of the liquid in the limb containing the positive electrode was also observed. The colourless liquid at the negative pole, when tested, was found to contain neither arsenic nor sulphuretted hydrogen.

A much more definite experiment was made with the use of a tube of the kind shown, having electrodes sealed into it at A and B. The tubes made use of are 30 cm. long. By the use of these tubes not only is the liquid to a large extent protected from the air, but any gaseous products of electrolysis are at once apparent, and the different actions of the two electrodes can be well studied.



Freshly prepared, strong, diffusible arsenic sulphide solution was introduced into the tube on Saturday. The solution contained about 11 grams of the sulphide per litre. A battery with an electromotive force of about 10 volts was connected with the electrodes, and a galvanometer placed in the circuit. A deflection of 1·25° was observed, corresponding, in the galvanometer used, to a current of about 0·000007 ampère.

On the actual experiment, a battery with electromotive force of 8 volts was used. At 2 P.M. on Saturday, the experiment was started. The negative pole was connected with A, the positive with B. The experiment was left over Sunday, and on Monday at 10 A.M., the sulphide was found to have been driven down 11·5 cm. By 1 P.M. it had been driven down 0·3 cm. further, a total of 11·8 cm. The rate of fall was now evidently becoming slower.

The repulsion being much greater from the negative pole, the current was now reversed at 1 p.m. to see whether the sulphide could be driven up again. By 4 P.M., the level of the sulphide surface had risen 2 cm. By Tuesday at 9 A.M., it had risen altogether 8·7 c.m. All this time there was absolutely no evolution of electrolytic gases. The battery was removed at 2.30 and again connected at 4.30 P.M. By Wednesday at 9 A.M., the total rise was 10·2 cm. It had now reached the positive electrode and the rate of rise which had at first been remarkably rapid, was now obviously much decreased. During Wednesday, the battery was connected up for 3½ hours without any further rise being observed, and on leaving it all night, the appearance remained exactly the same. The liquid round the negative pole was still coloured, thus showing a distinct difference from the action observed when the negative electrode was at the top.

On Thursday, the current was once more reversed. By Friday morning, the sulphide had been driven down 6·2 cm.

The liquid was now coagulated and tested for sulphuretted hydrogen and arsenious acid. No trace of either could be detected. One very small bubble of gas was now observed in the tube, the result of six days electrolysis.

Shellac.—Shellac does not dissolve in water, but it may be obtained in a state of pseudo-solution in that liquid by allowing a few drops of the alcoholic solution to fall into water. The shellac in this solution is repelled from the negative electrode.

Ferric Hydrate.—Some dilute colloidal ferric hydrate (dialysed) was similarly treated in a V-tube, the electrodes being 30 cm. apart. Left over night, the ferric hydrate was found to have been distinctly repelled from the positive electrode, the liquid in the corresponding limb of the tube being markedly paler in colour. At the same time, a very slight deposit of ferric hydrate was observed on the negative electrode.

Hæmoglobin.—Pure hæmoglobin crystals dissolved in water to a bright-red solution were treated in the same manner in a U-tube. The battery employed had an E.M.F. of about 8 volts. The electrodes were 13·5 cm. apart. The experiment was left over night, the tube being immersed in ice to prevent any spontaneous decomposition of the hæmoglobin. The hæmoglobin was markedly repelled from the positive electrode. In the corresponding limb, 4 cm. of colourless liquid was obtained, the hæmoglobin surface having sunk to that extent. At the same time, a small depression (0·5 cm.) had occurred in the opposite limb. The hæmoglobin thus repelled was examined spectroscopically. Throughout its extent it gave the normal absorption spectrum of oxyhæmoglobin. The apparently colourless liquid showed no absorption spectrum.

Magdala-Red.—In the case of Magdala-red, repulsion is observed from the positive electrode. With weak solutions, the liquid round the positive electrode becomes very nearly colourless. The experiments were performed in a U-tube. It was found that when a very strongly coloured solution was used, the Magdala-red obtained a certain concentration in the negative limb, and then no further action appeared to occur. With weak solutions, the experiment may be repeated many times without producing any change in the character of the Magdala-red. The colouring matter was dissolved in absolute alcohol, and the deflection of the galvanometer needle amounted in one case to about 0·25°, indicating a current of approximately 0·000001 ampère.

Several other liquids have been found to exhibit similar properties, but further details are reserved for a future occasion, when we hope to have more thoroughly investigated the subject.

In the earlier stages of these experiments the suggestion was an obvious one, that the phenomena observed were due to a change in state of aggregation of the substance present in the solution. As the experiments multiplied, this explanation became increasingly improbable, but as it is the one which, at first sight, seems most natural, it is necessary to have a considerable weight of evidence before rejecting it. We shall, therefore, here shortly state some of the considerations which seem to us to conclusively prove the above theory to be untenable.

1. If we are to suppose that the downward movement of the dissolved substance is the result of mechanical settling, due to formation of larger aggregates, these aggregates must be of comparatively enormous size. This is obvious in the case of the arsenious sulphide solution above referred to, for while suspensions containing visible particles sometimes take many months to settle, the above solution at first consists of particles so small as to be readily diffusible, and yet under electrical influence settles with great comparative rapidity. Moreover, these aggregates, if formed, must be again broken up on disconnecting the battery, since, then, not only does the downward movement cease, but the characteristic upward diffusion of the sulphide sets in. Now this subdivision of the larger aggregates is just one of the changes which, in the case of arsenious sulphide, we have found it impossible to effect. Thus arsenious sulphide β, in which we have been unable, as yet, to detect visible particles, cannot, apparently, be converted into arsenious sulphide γ. Furthermore, a concentrated solution of arsenic γ appears to contain somewhat larger aggregates than those of a dilute solution, though they are still quite

invisible. On diluting the strong solution, these do not seem to be broken up, for a solution so diluted is distinctly more fluorescent than a dilute solution directly obtained.

2. The upward movement of the sulphide, in the manner described, is similarly opposed to the theory, but it has been suggested that this is due to the removal of the upper surface of the liquid from the sphere of action of the negative electrode, consequent breaking up of the aggregates, and resulting liability to diffusion. Apart from previous considerations, this is opposed by the fact that the upward movement observed is entirely different, both in rapidity and character, from the ordinary diffusion of the sulphide. Thus the rise of level of 2 cm. in three hours, already described, would probably have occupied more than 24 hours in the case of simple diffusion. Moreover, in that case the sharply-defined surface of the concentrated solution steadily rose, with scarcely any of the shading off at the surface observed in ordinary diffusion.

3. That no formation of larger aggregates occurs in the case of Magdala-red, is plain from the following experiment. In a suitable apparatus, with electrodes about 2 cm. apart, the solution was treated electrically, while a ray of lime-light was passed between the electrodes. No polarisation of the scattered light could be observed. It is therefore obvious that no marked condensation had occurred.

In the case of Magdala-red, also, the concentration of the solution may be made to occur towards the upper or lower electrodes, according to the arrangement of the connections with the battery.

4. The remaining hypothesis, that the apparent repulsion may be due to decolorisation produced by the products of electrolysis, is obviously not in accord with the results obtained with arsenious sulphide. Indeed, when we consider how excessively small an amount of such products there must be (as deduced from the observed strength of current), we see that this hypothesis scarcely needs refutation. Obviously, it cannot be applied to such a case as that of shellac, and, to cite another instance, the behaviour of oxyhæmoglobin also disproves it. If decomposed, as suggested, it would not yield colourless products, but would show the spectrum of hæmatin.

5. Microscopical examination, so far as at present conducted, is in accord with the above arguments. An indigo suspension, in which the particles were well seen with a 1/5th objective, showed us these particles repelled rapidly from one electrode and attracted towards the other without any apparent change in the state of aggregation. Under similar influence, arsenic γ showed no visible particles, and, though we have not been yet able to examine the arsenic with a higher power, one would certainly expect particles capable of settling at the above described rate to be visible with the power employed.

It may be that the aggregates in these solutions are in an electrified condition, but on this subject it would be rash to dogmatise at present.

The only phenomenon in any way resembling the above with which we are acquainted is that, on passing a current through acidified water divided into two parts by a septum, the level of the water rises on that side of the septum at which the negative electrode is immersed (Porret). How far this phenomenon is really analogous to the above, we cannot say at present with any certainty.

THEORETICAL.

It seems to us that in the preceding part of this paper, we have made out at least a good *primâ facie* case for the belief that between obvious suspension and crystallisable solution there is no break in the series of grades of solution. We have seen that colloidal solution in many ways resembles liquid containing solid particles in suspension. We have seen that we can pass from solution in which these particles are visible under the microscope to those in which they are invisible, but indiffusible, and thence to those invisible and diffusible. These solutions show also gradations of permanency, and differ as to re-solubility. In some cases, such as arsenic sulphide, we cannot redissolve the solid after precipitation; in others, mercuric sulphide, starch, for example, we can readily effect re-solution. We are thus presented with varying degrees of action between the solvent and the solid. Further up the series we find evidence, as in silicic acid, of colloids in a still finer state of subdivision, and giving no positive evidence of the presence of solid particles. We then come to crystalloids, such as the compounds $9Fe_2O_3,FeCl_3$ and hæmoglobin, showing evidence of particles, yet by their ready re-solubility, permanence, and power to resist the influence of salts are evidently in a state of comparatively perfect solution. From these we pass to crystalloids in which no particles are discernible, but which are not electrolytes, and finally to those which are electrolytes. True fluorescent solutions show a luminous beam when a ray of light is passed through them, but the scattered light is not polarised. This kind of fluorescence is apparently unconnected with molecular complexity.

The electrical evidence is also of great interest from the point of view of the general theory of solution. We hope before long to present to the Society a further series of results on this subject, but we may here point out the similarity of behaviour exhibited, under this test, by more and less complex molecules. Colloidal arsenic sulphide is repelled from one of the electrodes in a similar manner to colloidal ferric hydrate, to hæmoglobin, and to Magdala-red. What the precise differences are in the different cases and in the case of electrolytes must be examined into on another occasion. We are here only concerned to point out the similarities.

From obvious suspension, then, we pass to colloidal solution, from colloidal solution to non-electrolytic crystallisable solution, and from these it is probably only one step further to electrolytic solutions, now often regarded as dissociated. This change may be regarded as continuous, and there is no reason to suppose that a sharp line separates the different states of matter from each other. The tendency of all modern investigation is to show that there are no such things as boundaries in nature, and in this case, like others, they seem to disappear on examination.

But it is obviously not a question of *mere* subdivision, nor can we regard the colloidal solution as cases of *mere* mechanical suspension. At one end of the series, where a powdered solid is kept temporarily suspended by being thoroughly shaken up with a liquid, there seems to be absolutely no action, except those of a purely mechanical kind, between the solid and the liquid wherein it is suspended. As, however, we pass up the series to matter in a more perfect state of suspension, it becomes impossible to avoid assuming *some* action, however slight and indefinite, of a more chemical nature between the liquid and the solid, which it retains in suspension. For instance, the fact that sulphuretted hydrogen water will split up precipitated mercuric sulphide into a state of subdivision so fine as to closely resemble ordinary colloidal solution appears inexplicable on a purely mechanical hypothesis. Some attraction, in its nature more resembling that of chemical affinity, there must surely be between water molecules or sulphuretted hydrogen molecules, or both, and the particles of mercuric sulphide. Passing further up the series, we may take as another example, the case of soluble starch. This substance dissolves without difficulty in water, but, as long suspected, and as further proved by our experiments, the starch exists in the solution in the form of finely-divided particles, and these are not in too fine a state of subdivision to be revealed by a ray of light. Such a result seems inexplicable, unless we assume something more nearly approaching chemical attraction between water and starch.

In the case of a solution of ferric hydrate in ferric chloride, there is no doubt whatever that a chemical attraction exists between solvent and solid. Not only is a definite crystalline compound of ferric oxide and chloride said to have been isolated, but, on coagulating a dialysed solution, which, as is well known, retains no inconsiderable amount of chloride, the chloride is found to be thrown out of solution along with the hydrate. But, with a large excess of chloride present, this solution shows a well-marked, luminous beam, the light of which is completely polarised. The solution appears to be perfectly permanent. The question naturally arises, In what manner is the ferric chloride in the solution combined with the hydrate? Are the aggregates revealed by a ray of light composed of the two components of the compound, or is the aggregate of ferric hydrate loosely combined with, or attracted by, the surrounding molecules of ferric chloride which are in more perfect solution? It is difficult to decide such a question; but it seems to us that probably both forms of combination occur at once. In the first case, we should have an example of mere mechanical suspension, unless we made the further supposition that the combined aggregates were loosely attracted by the water molecules in their neighbourhood. But the water molecules do not seem to exert so powerful an influence, for, on very prolonged dialysis and consequent gradual dissociation of the ferric chloride hydrate compound, the solution, as is well known, has a tendency to gelatinise on keeping. The simplest supposition appears, therefore, to be that the aggregates of ferric hydrate are held in solution almost entirely by their loose union with surrounding molecules of ferric chloride, themselves in a state of more perfect solution. The fact that it is not merely the more stably combined ferric chloride which assists solution is proved by the experiment of adding calcic chloride to the dialysed and undialysed liquid. In the former, precipitation is rapid; in the latter, it is far more difficult to produce. It certainly seems illogical to regard a solution of this kind as a case of mere mechanical suspension.

It may be remembered that the cases of certain sulphides soluble in sulphuretted hydrogen water present analogies to the present one. These sulphides (as shown in the paper "On some Metallic Hydrosulphides," p. 114) combine with a certain amount of sulphuretted hydrogen in the liquid in which they dissolve. The compound thus formed has, as a rule (see Mercuric Sulphide), a very complicated structure, and, in the case of these solutions, is often very unstable. On coagulating such a solution, however, the combined sulphuretted hydrogen is thrown out with the precipitate. A mercuric sulphide solution, when coagulated with calcic chloride, evolves no sulphuretted hydrogen (see also Copper). These cases entirely support the present view of colloidal solution. At the same time, the influence of salts in producing coagulation is difficult to explain.

The cases of albumen and of hæmoglobin are analogous. Albumens dried at 40° are re-soluble in water, and we must suppose a certain chemical attraction between solvent and solid. Hæmoglobin may be easily recrystallised and redissolved. Yet its solution reveals particles under the scrutiny of the beam.

It may be suggested that all that happens in these cases is a separation of these aggregates or molecules from the mass by virtue of their own vibratory motion, and that these small masses are able to support themselves in a liquid medium. Against this view must be set the non-diffusibility of some of the solutions such as starch. Besides this, such a theory is quite inadequate to account for the entirely different behaviour of different solvents towards the same solid. Starch, for instance, is not soluble in alcohol. Finally, in a case of mere mechanical suspension of very fine particles, must it not be supposed that in a very dilute suspension of this kind the particles would at least tend to settle with comparative rapidity to a concentration, at which the collisions with the lower vibrating particles would nearly counterbalance the tendency to further descent? Yet in many such dilute suspensions no such settling is observed. This may be partly accounted for by supposing the particles to be exceedingly minute; but in order to meet the requirements, a minuteness so extreme must be supposed (see Introduction, p. 150), that it is simpler to concede molecular attraction at once.

What, then, is the most rational way of regarding these phenomena of pseudo-solution and molecular solution? It seems to us by far the most simple course to suppose that in every case of so-called very fine suspension there is a certain degree of molecular attraction between the suspended solid and the solvent. The case of shellac affords a well-known example. According as this attraction is less or greater, the solution will be less or more permanent. Moreover, it is obvious that upon this attraction and that of the aggregates for each other, will depend the re-solubility of the solid. Shellac is not re-soluble. The water molecules do not attract the shellac aggregates with sufficient force to shake them asunder. On the other hand, in other cases, resolution is aided by mechanical agitation or boiling, &c., all of which favour the breaking up of the solid.

In cases where resolution is more readily effected (mercuric sulphide, albumen, hæmoglobin), either the particles of the solid are held together less firmly, or the attraction of the water molecules is greater. That the subdivision should proceed no farther than it does is easily accounted for by supposing, what is extremely probable, that the molecules of a solid are bound together in multiple aggregates which become looser with greater aggregation. These can be easily shaken asunder into their component aggregates of less complexity. But here the forces at work may be found powerless to produce further change. The less complex aggregates are bound together too firmly to be further dissociated, and, under certain circumstances, may be found acting as wholes. This explains why, in dissolving ferric hydrate in ferric chloride, the subdivision proceeds no farther than it does, and why a substance so readily soluble in water as neutral "Congo-red" yet reveals the presence of particles in its solution. It may here be noted, in support of these views, that gradual condensation to form aggregates of greater complexity may be observed in some cases. Thus colloidal antimony sulphide when freed from tartrate, shows a gradual and continuous condensation from aggregates quite invisible, through stages of increasing fluorescence, to aggregates visible under the microscope. The progress of a similar condensation is indicated by increasing fluorescence in antimony sulphide solutions after keeping for some months. Silicic acid presents us with a case of similar regular condensation. In the case of chromic chloride, we have probably an example of the gradual breaking up of aggregates through the various stages of pseudo-solution till crystallisable solution is arrived at. The precise analogy between this and that of antimony sulphide in the reverse direction makes us think it probable that we are here following a continuous breaking up of molecular aggregates.

It may be observed that, if these views are correct, we have here an interesting analogy between the lower and higher grades of solution. For, whilst in the lower grades we have combination between very large aggregates of the dissolved substance and the water molecules in their neighbourhood, it has been shown with great probability by Pickering and others that in the case of some of the higher grades of solution the molecules of the dissolved substance combine with a large number of water molecules to form very high hydrates. This does not seem to us to affect the question of probable dissociation into ions in the most perfect solution.

Throughout the above argument we have necessarily been assuming, what must now be fully stated, that these fine particles revealed by the luminous beam are simply large molecular aggregates, and retain many of their molecular properties. As wholes they can enter into loose combination, and as wholes they can attract each other with gradual formation of larger aggregates.

These molecular aggregates may even attain a complexity so great that they become visible under the microscope, and yet do not entirely lose their molecular properties (mercuric sulphide). What then is the interpretation of the continuous vibratory movement of these aggregates as seen under the microscope? Enormous as must in all probability be the number of molecules associated to form a visible aggregate, yet as the transition from them to states of undoubted molecular subdivision seems perfectly continuous, we can scarcely avoid the conclusion that this vibratory motion is one of the molecular properties still retained by them, and that what we are here observing is simply molecular vibration. On the other hand, it might be conceived that these oscillations are due to the impacts of the liquid molecules. On the whole this seems less probable, for considering the relative sizes of the particles and the water molecules, it seems doubtful whether these impacts would occur with sufficient irregularity to cause visible motion. Furthermore, there is no proof of the existence of large molecular aggregates of water which would be competent to produce such effect. The conclusion that we are here actually observing molecular vibration seems a rash one, but it appears at present to be in accordance with facts, and to offer the most rational explanation of Brownian movement.

As to the electrical portion of our work, we shall not at present offer any theory, though the subject is an obviously tempting one for speculation. But on this point, and on the general question discussed in this paper, we hope in a short time to have more results to communicate.

Our main conclusion, therefore, is that from first to last, from pseudo-solution to crystalloidal solution, we are concerned with chemical as well as with physical forces, and that the progress from the lower to the higher terms of the series is accompanied by increasing fineness of subdivision of the dissolved matter, and by increasing definiteness in the action of the chemical forces.

SUMMARY.

We shall here briefly review in outline the main results of this and the preceding paper.

I. *Experimental.*—1. The following inorganic colloidal solutions reveal particles visible under the microscope:—

Mercuric sulphide, arsenious sulphide (α).

2. The following inorganic colloidal solutions contain the dissolved substances in states of aggregation recognisable by optical or other means:—

All colloidal sulphide solutions.
Ferric hydrate, chromic hydrate, aluminium hydrate, silicic acid.

3. Owing to the difficulty of preparing organic colloids in a state of purity, only the following have, as yet, been examined. They all exhibit a state of subdivision not too fine to be recognised by the methods employed:—

Cellulose, starch, Congo-red (acid and neutral).
[Alkaline Congo-red is in a state of much more perfect solution.]

4. The following colloids exist in solution in a state of subdivision too fine for the aggregates to be detected by ordinary methods:—

Molybdic acid, silicic acid (in presence of hydrochloric acid).

5. The following crystallisable solutions reveal molecular aggregates large enough to be detected by optical or other methods:—

Ferric hydrate in ferric chloride (said to crystallise as $9F_2O_3,FeCl_3$).
Oxyhæmoglobin, carbonic oxide hæmoglobin.

6. Silicic acid, after dialysis, begins to exhibit signs of advancing molecular condensation. This is analogous to the case of antimony sulphide, in which the steady molecular condensation is under certain circumstances perfectly demonstrable (see above).

Chromic chloride, when first dissolved, appears to exist in the form of large aggregates, which are gradually broken up with final formation of crystallisable solution.

II. *Theoretical.*—We consider that we have made out a good *primâ facie* case for the belief that there is a continuous series of grades of solution passing without break from suspension to crystallisable solution. In the lowest grades of solution, a certain loose attraction exists between the "suspended" particles and the molecules of the solvent. This conclusion is in accordance with the experimental evidence. The very finely divided particles in the lower grades of solution are simply large molecular aggregates retaining many of their molecular properties. In passing up the series through the different grades of solution, these aggregates on the whole become smaller, or, at least, consist of a smaller number of molecules, and the forces by which they are held in solution become more definitely those of chemical attraction.

III. *Electrical Behaviour of certain Solutions.*—Mention has been made in the paper of a new property of certain solutions. It seems to hold with a wide range of solutions extending from suspension to crystalloidal solution. This property consists in the repulsion of the dissolved substance *as an unaltered whole* from one of the electrodes of a battery if these be immersed in the solution. In the case of colloidal arsenic sulphide, the sulphide aggregates are repelled from the negative electrode. They are also repelled, but much less strongly, from the positive electrode. Crystalloidal Magdala-red dissolved in absolute alcohol is repelled from the positive electrode. In this case there seems to be no repulsion from the negative. This property is of much interest in itself, and may prove of much value in connecting the higher grades of solution.

Researches on the above subjects are now in progress.

In conclusion, we wish to express our hearty thanks to Professor Ramsay, who has most kindly encouraged and advised us throughout the whole of the work of the three preceding papers. It is with sincere pleasure we acknowledge that without his kind help it would have been difficult to bring these researches to a satisfactory issue.

We should like also, among others, to thank Professor Carey Foster for kind assistance in the electrical portion of our work, and Professor E. A. Schäfer for placing his microscope at our disposal.

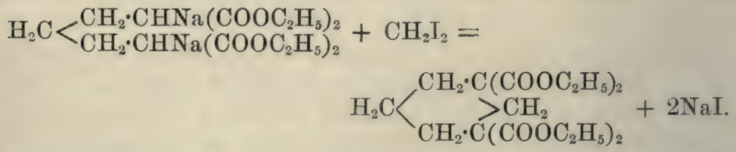
University College,
London.

XII.—CONTRIBUTIONS FROM THE LABORATORIES OF THE HERIOT WATT COLLEGE, EDINBURGH.

Synthesis of Hexahydroterephthalic Acid.

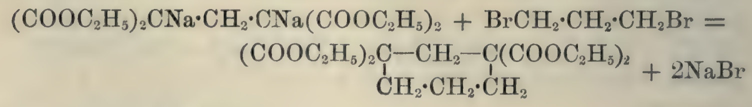
By J. E. MACKENZIE, B.Sc., and W. H. PERKIN, Jun., Ph.D., F.R.S.

IN a paper published a short time since (Trans., 1891, **59**, 798), it was shown that the disodium compound of ethyl pentanetetracarboxylate, when digested in alcoholic solution with methylene iodide at 100° is, in part, converted into ethyl hexamethylene tetracarboxylate [1 : 1 : 3 : 3], thus:—



$$H_2C<\begin{matrix}CH_2\cdot CHNa(COOC_2H_5)_2\\ CH_2\cdot CHNa(COOC_2H_5)_2\end{matrix} + CH_2I_2 = H_2C<\begin{matrix}CH_2\cdot C(COOC_2H_5)_2\\ CH_2\cdot C(COOC_2H_5)_2\end{matrix}>CH_2 + 2NaI.$$

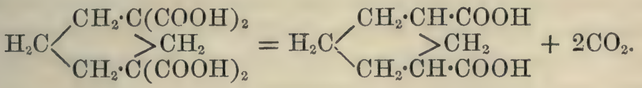
The same ethereal salt is also produced by the action of trimethylene bromide on the disodium compound of ethyl propanetetracarboxylate,



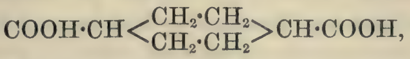
$$(COOC_2H_5)_2CNa\cdot CH_2\cdot CNa(COOC_2H_5)_2 + BrCH_2\cdot CH_2\cdot CH_2Br = \begin{matrix}(COOC_2H_5)_2C-CH_2-C(COOC_2H_5)_2\\ |\qquad\qquad |\\ CH_2\cdot CH_2\cdot CH_2\end{matrix} + 2NaBr$$

(Trans., 1891, **59**, 990).

This ethereal salt, on hydrolysis, yields the corresponding tetrabasic acid, and this, when heated at 200—220°, yields a mixture of the two isomeric Γ^{cis} and $\Gamma^{cistrans}$ hexamethylenemetadicarboxylic acids (hexahydroisophthalic acids), with elimination of 2 mols. of carbonic anhydride, thus :—

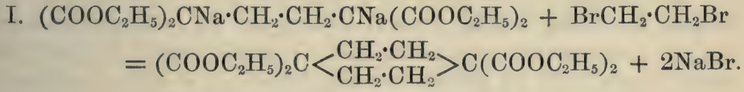


During the course of the experiments, it was thought probable that the two isomeric hexahydroterephthalic acids,



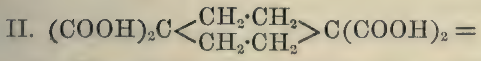
$$\mathrm{COOH{\cdot}CH}\!<\!\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\!>\!\mathrm{CH{\cdot}COOH},$$

which Baeyer prepared in the course of his beautiful investigations on the reduction of terephthalic acid (*Annalen*, **245**, 169—174), might be synthetically produced in a similar way, from the ethereal salt formed by the interaction of the disodium compound of ethyl butanetetracarboxylate with ethylene bromide, thus :—



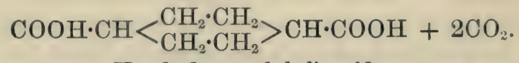
$$\text{I. } \mathrm{(COOC_2H_5)_2CNa{\cdot}CH_2{\cdot}CH_2{\cdot}CNa(COOC_2H_5)_2 + BrCH_2{\cdot}CH_2Br}$$
$$= \mathrm{(COOC_2H_5)_2C}\!<\!\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\!>\!\mathrm{C(COOC_2H_5)_2 + 2NaBr.}$$

Ethyl hexamethylenetetracarboxylate [1 : 1 : 4 : 4].



$$\text{II. } \mathrm{(COOH)_2C}\!<\!\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\!>\!\mathrm{C(COOH)_2} =$$

Hexamethylenetetracarboxylic acid.



$$\mathrm{COOH{\cdot}CH}\!<\!\begin{matrix}\mathrm{CH_2{\cdot}CH_2}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}\!>\!\mathrm{CH{\cdot}COOH + 2CO_2}.$$

Hexahydroterephthalic acid.

On making the experiment, it was found that a considerable quantity of the sparingly soluble $\Gamma^{cistrans}$ hexahydroterephthalic acid was produced in this way, and from the mother liquors of this acid a small quantity of an acid melting at 159—162° was with difficulty isolated ; the latter is probably the corresponding Γ^{cis} acid, which melts at 161—162°. Unfortunately, it was not possible to obtain sufficient of the second acid for analysis, owing to the difficulty of preparing ethyl butanetetracarboxylate in large quantities.

This ethereal salt, the preparation of which has been given in a previous paper (Trans., 1887, **51**, 19), is produced in very small quantities when ethylene bromide acts on the sodium compound of ethyl malonate, thus :—

$$\mathrm{2(COOC_2H_5)_2CHNa + BrCH_2{\cdot}CH_2Br =}$$
$$\mathrm{(COOC_2H_5)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOC_2H_5)_2 + 2NaBr;}$$

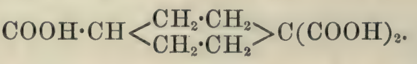
but, in spite of numerous experiments instituted with the object of improving the yield, the largest amount which has as yet been obtained was 35 grams from 1 kilo. of ethyl malonate. For this reason, it was not possible to follow the course of the reaction between the disodium compound of this ethereal salt and ethylene bromide through all its stages, as was the case in the experiments on the synthetical formation of the hexahydroisophthalic acids.

The synthesis of hexahydroterephthalic acid was carried out briefly as follows:—

4 grams of sodium was dissolved in 60 grams of absolute alcohol; the well-cooled solution mixed with 30 grams of pure ethyl butanetetracarboxylate, 17 grams of ethylene bromide added, and the whole heated in a soda-water bottle at 100° for 10 hours.

The product, which was brownish, and smelt distinctly of ethylene bromide, still had a strongly alkaline reaction; it was mixed with water, extracted four times with ether, the ethereal solution washed well with water, dried over calcium chloride, evaporated, and the residual brownish oil (23 grams) hydrolysed by boiling with a mixture of concentrated sulphuric acid (1 part), water (1 part), and glacial acetic acid (2 parts) for six hours in a reflux apparatus. Steam was next passed through the boiling liquid until all the acetic acid had been removed, the pale-brownish solution cautiously concentrated on a water-bath, and then extracted 30 times with ether. The ethereal solution, after being dried over calcium chloride and evaporated, left 12 grams of a thick, oily acid, which, on standing over sulphuric acid under diminished pressure, rapidly deposited crystals; these, after washing with ether, in which they are sparingly soluble, crystallise from water in cauliflower-like masses, which melt approximately at 152—153°.

The results of the analysis indicate that this substance is hexamethylenetricarboxylic acid,



$$COOH{\cdot}CH{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}C(COOH)_2.$$

0·1410 gram substance gave 0·0800 gram H_2O and 0·2572 gram CO_2.

	Theory. $C_9H_{12}O_6$.	Found.
C.......	50·00 per cent.	49·75 per cent.
H	5·55 ,,	6·30 ,,
O.......	44·44 ,,	43·95 ,,

Owing to the small amount of material at our disposal, no further experiments could be made with this acid, and for this reason, it must in the meantime remain doubtful whether this view of the constitution of this substance is correct.

The remainder of the crude acid was heated at 200—220°, until all evolution of carbonic anhydride had ceased, and the thick, brownish residue, which became almost solid even while quite hot, was allowed to remain in contact with a porous plate for some days; it was then dissolved in dilute sodium carbonate solution, and digested with freshly ignited animal charcoal for two or three hours. The filtered solution after evaporating to a small bulk, and acidifying with hydrochloric acid, deposited on standing about 1·3 grams of a granular precipitate; this, on examination, was found to consist of almost pure $\Gamma^{cistrans}$ hexahydroterephthalic acid. The substance, after recrystallisation from water, gave the following numbers on analysis :—

0·1434 gram substance gave 0·0920 gram H_2O and 0·2933 gram CO_2.

	Theory. $C_8H_{12}O_4$.	Found.
C	55·81 per cent.	55·77 per cent.
H	6·98 ,,	7·12 ,,
O	37·21 ,,	37·11 ,,

This acid melts approximately at 300°, but not sharply; when strongly heated, it sublimes, and this behaviour was especially well observed during the combustion of the substance, when almost the whole sublimed and was deposited in glistening crystals on the cooler portions of the tube. It is readily soluble in warm water, but much more sparingly in cold water; the solution of the sodium salt of the acid does not decolorise potassium permanganate even on standing for some time.

In order, however, to prove conclusively that this acid was identical with the $\Gamma^{cistrans}$ hexahydroterephthalic acid obtained by Baeyer from terephthalic acid, the methyl salt was prepared according to Baeyer's directions.

About 0·2 gram of the acid was gently heated in a test-tube with an excess of phosphorus pentachloride for a few seconds, allowed to cool, and the residual solid mass mixed with methyl alcohol. The product was poured into water, the crystalline mass which separated collected, washed with water, and dried on a porous plate over sulphuric acid under diminished pressure. The resulting glistening, crystalline mass melted at 66—68°, and after recrystallisation from light petroleum at 69—70°; Baeyer gives 71° as the melting point of the dimethyl salt of $\Gamma^{cistrans}$ hexahydroterephthalic acid.

The mother liquors from the above acid were evaporated to a very small bulk, allowed to stand for some days, the crystalline mass which separated, collected, washed with a little water, and dried on a porous plate at 100°. The resulting crude substance, which, when heated in a capillary tube, began to melt at 145°, and was not completely melted at 190°, was separated into three substances by conversion into the calcium salt, and repeated recrystallisation of the acids from water: that is, into small quantities of Γ^{cistrans} hexahydroterephthalic acid, a considerable quantity of an acid melting at 147—149°, probably adipic acid (from the hydrolysis of some unchanged ethyl butanetetracarboxylate), and about 0·028 gram of an acid melting at 159—162°, which is probably Γ^{cistrans} hexahydroterephthalic acid (m. p. 161—162°).

The titration of this acid gave the following results :—

0·0271 gram required for neutralisation 3·1 c.c. of potassium hydrate solution (1 c.c. = 0·00559 gram KOH) = 0·0173 gram KOH.

A bibasic acid of the formula $C_8H_{12}O_4$ requires theoretically 0·0177 gram KOH.

The solution of the potassium salt of this acid, rendered slightly alkaline by the addition of potassium carbonate, did not decolorise potassium permanganate solution.

XIII.—*Investigation of the Change proceeding in an Acidified Solution of Sodium Thiosulphate, where the Products of the Change are retained in the System.*

By ARTHUR COLEFAX, B.A., Ph.D., Student of Christ Church, Oxford.

Object of the Work.

IN undertaking the work an account of which is given in this paper, the objects in view were:

I. To ascertain whether thiosulphuric acid is capable of existence.
II. To investigate the nature of the change, and the conditions under which it proceeds, when sodium thiosulphate is acidified.

A Short Account of the Literature bearing on the Subject.

Flückiger (*Jahresbericht*, 1863, 149) states that, in flowers of sulphur and even in sulphur recrystallised from carbon bisulphide, traces of thiosulphuric acid are to be found. He showed that by the action of an aqueous solution of sulphur dioxide on flowers of sulphur, traces of the acid were formed. If the sulphurous acid and sulphur were heated together in sealed tubes at a temperature of 80—90°, the reaction went more easily.

J. Myers (*Compt. rend.*, **74**, 195) says that the action of steam on sulphur produces thiosulphuric acid, and not pentathionic acid as Mulder had stated.

H. Rose (*Traité de Chimie Analytique*, p. 475) remarks that, in acidified solutions of thiosulphates, provided the solutions be not too dilute, the decomposition of thiosulphuric acid is not complete even after several weeks.

Salzer (*Ber.*, **19**, 1696), in a paper on "a new method of formation of the so-called pentathionic acid," says that the iodine titration method affords a means of proving that the decomposition of acidified thiosulphates into sulphurous acid and sulphur becomes complete.

Landolt (*Ber.*, **16**, 2958): "Time of existence of thiosulphuric acid in aqueous solutions." The method followed was, to observe the first appearance of opalescence, and note the time that elapsed between its appearance and the acidification of the thiosulphate solution. His results may be briefly summarised.

The time elapsing before the appearance of the opalesence is,

I. Independent of the nature of the acidifying acid.
II. Uninfluenced by excess of either acid or thiosulphate.
III. Independent of the quantity of solution used.
IV. Influenced by the actual concentration, and also by the temperature.

Method of Investigation.

In the text-books (for example, Roscoe and Schorlemmer, p. 348) it is stated that thiosulphuric acid, produced by the acidification of thiosulphates, undergoes decomposition according to the equation,

$$H_2S_2O_3 = H_2SO_3 + S.$$

At the outset an experiment was made in order to ascertain whether or not, under the most favourable conditions, the decomposition of thiosulphuric acid is complete. The conditions which appeared most favourable were to have some excess of acid, an elevated temperature, and the removal of the sulphurous acid as it was formed. Accordingly, 1 gram of sodium thiosulphate was dissolved in boiled water, and the solution washed into a distillation flask; 20 c.c. of dilute hydrochloric acid were added, and the distillation proceeded with; the evolved sulphur dioxide was absorbed by chlorine-water contained in the receiver, and was estimated as barium sulphate,

$BaSO_4$ = 0·9172 gram = per cent. S as SO_2 12·60 instead of 12·90.

Here, it may be taken that the decomposition is complete.

In the investigation of the change, where the products are not eliminated from the system in which they are found, the method employed is as follows:—

A solution of sodium thiosulphate containing a known weighed quantity of the pure recrystallised salt $Na_2S_2O_3,5H_2O$, is dissolved in a known volume of distilled water, which has been boiled and allowed to cool in a stream of hydrogen gas to expel all air. An acid, whether hydrochloric or sulphuric, is then made by dilution with similarly prepared distilled water, of such a strength that in 1 c.c. there is a quantity of acid exactly sufficient for the saline decomposition of the quantity of thiosulphate contained in 1 c.c. of its solution. An iodine solution is also made of such a strength that it will react with about half its own volume of the thiosulphate solution, but its exact strength is not determined.

Hence, the extent to which the thiosulphuric acid has suffered decomposition can be ascertained from a knowledge of the increase in the iodine titration, provided no sulphurous acid is lost, and that no interaction of thiosulphuric acid and sulphurous acid takes place. Loss of sulphurous acid will result in the decomposition being regarded as less complete than it is in reality.

Having made the solutions of sodium thiosulphate and acid, they are titrated with, and their strengths determined in terms of, the iodine and an ammonia solution, respectively. The reason for ascertaining the strength of the acid in terms of an ammonia solution will be explained in the sequel.

It may be here remarked that no alteration occurs either in the iodine titration or in the ammonia titration on mixing the solutions of sodium thiosulphate and acid; that is, 10 c.c. of the sodium thiosulphate solution, when acidified with 10 c.c. of the solution of the acid, possess immediately after mixing the same titration in terms of the iodine that they did before acidification. The same is true of the acidity titrations. The presence of free sulphur in a solution of sulphurous acid did not affect its iodine titration.

About 100 c.c. of each of the solutions, sodium thiosulphate and acid, are run into two clean and dry flasks, which are then placed in the bath, where they remain until the solutions have attained the temperature of the bath. Into a third dry flask, 50 c.c. of a sodium thiosulphate solution, which has been brought to the requisite temperature, are run, and afterwards 50 c.c. of the acid; the time at which the addition of acid is completed is recorded; 10 c.c. of the acidified thiosulphate solution are then withdrawn by means of a pipette, which was used throughout the whole of the experiments, and run into a small glass bulb, from which the air had been displaced by carbonic acid. It was found that with the strongest solutions, three, and with the weaker, six to nine, such bulbs could be filled before the first appearance of opalescence in the acidified solution occurred. When the bulbs are so filled they are sealed before the blowpipe, placed in the bath, and allowed to remain the desired time. At the expiration of this period, the bulb, after being rinsed with distilled water, is broken in a known volume of iodine solution mixed with some boiled water contained in a pedestal test-glass, whose sides are thin and as colourless as possible. The quantity of iodine taken was always about 1 c.c. short of that which experience showed was necessary for the complete titration of the contents of the bulb.

In order that the bulbs might be of nearly equal capacity, they were blown in a mould, which consisted of two copper hemispheres, one of which was provided with an aperture through which the molten end of the glass tube could be introduced. The rims of the hemispheres were fastened together with a little Faraday's cement. The moment the heated sides of the glass bulb touch the inside of the copper sphere, the cement is melted by the heat, the two hemispheres come apart, and the bulb is formed of the requisite size.

To my friend and colleague, Mr. A. G. Vernon Harcourt, I am indebted for the suggestion and device of this mould.

Consideration of the possible Sources of Error in the Method.

The principle of the method which has already been described as the one employed in these experiments is that the titration of the sulphurous acid produced by the decomposition of a quantity of thiosulphuric acid, taken in terms of the iodine solution, is the double of the titration of the same quantity of thiosulphuric acid before change.

The justification of this principle rests upon the verification of the equations :—

$$H_2S_2O_3 = H_2SO_3 + S.$$
$$2H_2S_2O_3 + I_2 = H_2S_4O_6 + 2HI.$$
$$H_2SO_3 + H_2O + I_2 = H_2SO_4 + 2HI.$$

There are several possible sources of error which must be estimated before the results of these experiments can allow of deductions being drawn from them. They may be stated as :—

1. Oxidation of a part of the sulphurous acid formed.
2. Titration complications.
3. Incompleteness of saline decomposition.

I. *Oxidation of Sulphurous Acid.*—The sulphurous acid formed in the decomposition of thiosulphuric acid becomes partly oxidised; any attempt to measure the extent of decomposition by means of a comparison of the iodine titration before and after the change must be deceptive. This possible source of error was examined into as follows:—

Four bulbs were charged with carbonic acid, and 10 c.c. of a solution of sulphurous acid run into each. They were then sealed and placed in the bath and allowed to remain 24 hours. At the end of this time, the bulbs were broken under water and titrated with an iodine solution.

10 c.c. of the H_2SO_3 solution previous to introduction into the bulbs, required 9·00 c.c. of an iodine solution.

At the end of the 24 hours:—

Bulb......	I.	II.	III.	IV.
Required of iodine solution ..	9·00	9·05	9·00	9·05

The solution of sulphurous acid was made with boiled water which had been cooled in a current of hydrogen.

From these experiments, it will be seen that oxidation of the sulphurous acid formed by the decomposition of thiosulphuric acid, under the conditions of experiment which hold in the method employed, seems improbable.

The second method by which this possible source of error could be estimated was suggested by the following considerations:—Whenever sulphurous acid is titrated with iodine, a development of acidity takes place; hydriodic acid is produced together with sulphuric acid, the latter being formed in quantities exactly equivalent to the sulphurous acid, thus:—

$$H_2SO_3 + H_2O + I_2 = 2HI + H_2SO_4.$$

Hence, for the same solutions of alkali and iodine the ratio between the iodine titrations and the acidity titrations after the addition of iodine will be a constant. The value of this constant, for the ammonia and iodine solutions used, was determined by means of a pure solution of sulphurous acid. This solution of sulphurous acid was made by driving, by means of a stream of hydrogen gas, sulphur dioxide into boiled distilled water, which had been cooled in hydrogen. In the case, then, of the decomposition of thiosulphuric acid, unless the increase in the iodine titration and the development of acidity after titration with iodine, bear to one another a ratio expressed by the above-determined constant, the equation

$$H_2S_2O_3 = H_2SO_3 + S$$

does not represent the entire change; oxidation of sulphurous acid, or, may be, the formation of a polythionic acid by the interaction of sulphurous and thiosulphuric acids, has taken place.

In what has been said above, it has been supposed that none of the titration complications to be considered under the second of the sources of possible error has supervened.

II. *Titration Complications.*—In view of the statement of Spring (*Ber.*, 1873, 1108), that sodium trithionate is formed by the action of iodine on a mixture of the sodium salts of sulphurous and thiosulphuric acids, it was necessary to make sure that no such formation of trithionic acid takes place when a mixture of thiosulphuric and sulphurous acids is titrated with iodine.

Spring represents the reaction by which sodium trithionate is formed thus:—

$$Na_2S_2O_3 + Na_2SO_3 + I_2 = 2NaI + Na_2S_3O_6.$$

Before attempting to ascertain whether a corresponding change happens in the case of a mixture of sulphurous and thiosulphuric acids, the action of iodine on a mixed solution of sodium sulphite and thiosulphate was investigated.

Experiment No. 1.—10 c.c. of a solution of neutral sodium sulphite, Na_2SO_3, required 10·85 c.c. of a solution of iodine; 10 c.c. of a solution of sodium thiosulphate required 9·75 c.c. of the iodine solution.

A solution containing 10 c.c. of the sodium sulphite and 10 c.c. of the thiosulphate required 20·60 c.c. of the iodine solution, or no trithionate is formed.

Experiment No. 2.—A solution of sulphite of sodium in boiled water was made.

10 c.c. required 18·95 c.c. of iodine solution, and the acidity after iodine titration required 2 c.c. of a solution of ammonia.

10 c.c. of a solution of sodium thiosulphate required 9·80 c.c. of the iodine solution, and there was no development of acidity.

The mixed solution, containing 10 c.c. of each of the above solutions, required 28·70 c.c. iodine, and the acidity developed 2 c.c. of ammonia solution.

A solution of sodium hydrogen sulphite gave an exactly similar result. Hence, under these conditions, not a trace of sodium trithionate is formed.

Starch was the indicator used in the iodine reaction, and methyl-orange was employed in the acidity reaction. Before adding the methyl-orange, the blue starch iodide colour was discharged by a drop of a thiosulphate solution.

Proceeding on precisely similar lines, it was shown that the iodine titration of a mixed solution of sulphurous acid and sodium thiosulphate is the sum of the iodine titrations of the constituents, and that the same was true of a mixed solution of sulphurous and thiosulphuric acids.

Hence, under the conditions of experiment, the sulphurous acid produced by the decomposition of thiosulphuric acid does not become oxidised, and the extent of the change of thiosulphuric acid into sulphurous acid and free sulphur can be estimated by employing the iodine titration. Moreover, the ratio between the increase in iodine titration and the development of acidity after titration with iodine, can be employed to show whether oxidation, or the formation of a polythionic acid by interaction of sulphurous and thiosulphuric acids, has taken place.

III. *Incomplete Saline Decomposition.*—This has been named as the third possible source of error. If the reaction

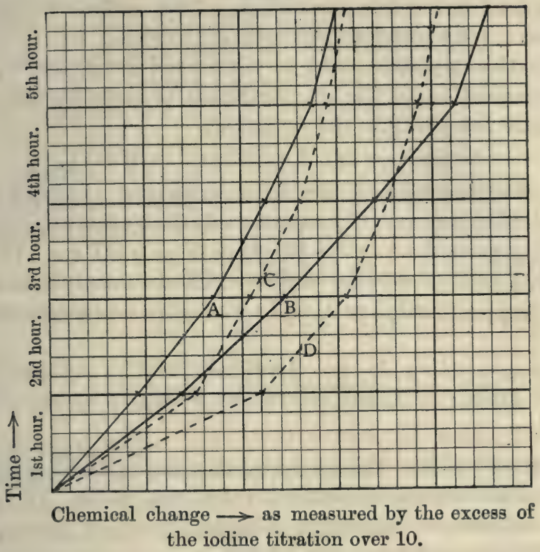
$$2HCl + Na_2S_2O_3 = 2NaCl + H_2S_2O_3$$

proceeds but imperfectly, the increase in the iodine titration might never become the double of the original titration before acidification, because, the conversion of sodium thiosulphate into thiosulphuric acid not being complete, the change of thiosulphuric acid into sulphurous acid and free sulphur could never proceed so far that the sulphurous acid thus formed possessed a titration the double of that of the thiosulphate of soda originally acidified.

With a view to estimate how far the saline decomposition is complete, a comparison of the chemical change taking place in solutions of barium thiosulphate and of sodium thiosulphate of approximately equal concentration, each acidified with hydrogen sulphate, was made. The result of this comparison is shown in Fig. 1. It is evident that with solutions of barium thiosulphate and sodium thiosulphate, when acidified with a quantity of sulphuric acid the equivalent of the salt present, the curves marking the progress of the change of thiosulphuric acid into sulphurous acid and free sulphur are similar, and the extent of the change at the end of the fifth hour is approximately equal in the two cases. However, it is noticeable that the change proceeds further in the system $Na_2S_2O_3 + H_2SO_4$, the one in which complete saline decomposition is not assured by the conditions of experiment.

In the case where twice the equivalent quantity of acid is used, the decomposition of thiosulphuric acid proceeds still further in both cases, but the system $BaS_2O_3 + H_2SO_4$ is now the one where the change goes farthest. This is probably explicable by the formation of sodium hydrogen sulphate with a portion of the sulphuric acid, and so the ratio of free acid to salt is not as great as in the case of the barium thiosulphate and sulphuric acid reaction.

FIG. 1.



A and B represent the curves tracing the chemical change as given by the excess over the initial titration for the system BaS_2O_3, H_2SO_4 during the first five hours. C and D (the dotted lines) the same for the system $Na_2S_2O_3 + H_2SO_4$ of the same initial titration. $t = 30°$ C.

With the system $BaS_2O_3 + H_2SO_4$, it was noticed that a peculiar occlusion of a portion of the liquid by the precipitated barium sulphate took place. For example, 10 c.c. of the barium thiosulphate solution, before acidification with sulphuric acid, possessed a titration 16·85 c.c. of an iodine solution, but after acidification its titration fell to 16·30. The initial titration of the barium thiosulphate solution was therefore taken *when acidified*, in the comparison with the system $Na_2S_2O_3 + H_2SO_4$.

A second method of ascertaining how far the saline decomposition is complete was the following:—A solution of sodium thiosulphate was acidified with the equivalent quantity of acid (hydrochloric acid), and placed in a shallow dish over caustic soda solution in a vacuum. By this means, the sulphurous acid formed was eliminated from the system, and, therefore, if the whole of the thiosulphuric acid became converted into sulphur and sulphurous acid, the titration would, if the saline decomposition were complete, finally equal *nil*. It was found that the iodine titration of the solution, from being 9·8 c.c. iodine solution, sank at the end of 16 days to 0·35 c.c. iodine solution. As the solution becomes more dilute in respect of thiosulphuric acid, the decomposition into sulphur and sulphurous acid proceeds very slowly. However, the experiment gave promise of almost complete, if not complete, saline decomposition. This suffices for the purpose of this work. Where the sulphurous acid formed by the decomposition of the thiosulphuric acid is eliminated from the system, the saline decomposition of the thiosulphate of soda by the acidifying acid, proceeds according to the equation,

$$Na_2S_2O_3 + 2HCl = 2NaCl + H_2S_2O_3.$$

In another experiment on the lines described above, it was found that the acidified sodium thiosulphate solution, after the expiration of a fortnight, possessed an iodine titration of only 0·1 c.c. In this latter experiment, a smaller volume of the acidified thiosulphate was taken, and so the escape of sulphur dioxide was more easily effected.

The Change proceeding in an Acidified Solution of Sodium Thiosulphate attains a Limit where the Products of the Change are retained.

A solution of sodium thiosulphate, containing 4·885 grams of the salt dissolved in 500 c.c. of distilled water, was made. The acidifying acid was a solution of hydrogen chloride, 30 c.c. of which, on precipitation with silver nitrate, gave 0·3432 gram of silver chloride. The strength of the acid solution was further determined by titrating with a solution of sodium carbonate containing 4·1760 grams of the pure dry salt per litre, using methyl-orange as an indicator. 10 c.c. of the acid required 10·10 c.c. of the sodium carbonate solution. These results gave as the strength of the hydrogen chloride solution—

I. 10 c.c. contain 0·02909 gram HCl (as determined by precipitation with $AgNO_3$).

II. 10 c.c. contain 0·02904 gram HCl (as determined by titration with Na_2CO_3).

The theoretically equivalent quantity requisite for the complete saline decomposition of a solution of sodium thiosulphate containing 4·885 grams of the crystallised salt in 500 c.c. is 0·02876 gram HCl per 10 c.c. The water used in the preparation of these solutions was boiled distilled water which had been cooled in a stream of hydrogen.

10 c.c. of the solution of sodium thiosulphate required 19·75 c.c. of a solution of iodine containing approximately 2·5 grams of iodine dissolved in 1 litre of water. 10 c.c. of the acid required 20·30 c.c. of a solution of ammonia, using methyl-orange as indicator. Hence 10 c.c. of a solution containing equal volumes of the sodium thiosulphate and hydrogen chloride solutions should possess a titration in terms of the iodine solution of 9·875 c.c., and in terms of the ammonia solution a titration of 10·15 c.c. This was found to be true immediately after mixing.

Some of the glass bulbs, from which the air had been displaced by carbonic acid, were charged with 10 c.c. of the acidified solution of sodium thiosulphate, and placed in a bath maintained constant at a temperature of 30°. At the end of certain intervals from the time of mixing, the contents of a bulb were titrated with the iodine solution, and the acidity, *after titration with iodine*, determined in terms of the ammonia solution. The blue colour of the starch iodide was discharged by a drop of a solution of sodium thiosulphate before the addition of the (indicator) methyl-orange.

At the end of the ..	1st hr.	2nd hr.	3rd hr.	4th hr.	5th hr.	24th hr.	48th hr.
The iodine required was	13·1	14·0	14·8	14·9	15·0	15·30	15·30 c.c.
And the ammonia required was....	13·15	14·20	14·95	15·10	15·20	15·55	15·50 ,,

Hence a limit value is reached within 24 hours of the time of mixing the solutions of sodium thiosulphate and hydrogen chloride.

That no oxidation or formation of a polythionic acid had occurred was shown from the following considerations :—A solution of sulphurous acid, prepared as described, gave a ratio between its iodine titration and the acidity titration after the addition of iodine, $\frac{38·85}{38·30} = 1·0143$.

Hence, if no oxidation of sulphurous acid or formation of a polythionic acid had occurred—

(The acidity titration − 10·15) × 1·0143 should equal, when added to the original iodine titration (9·875), the observed iodine titration The values so obtained gave—

1st hour (13·15 − 10·15) × 1·0143 + 9·875 = 12·92 instead of 13·1
2nd ,, (14·20 − 10·15) × 1·0143 + 9·875 = 13·98 ,, 14·0
3rd ,, (14·95 − 10·15) × 1·0143 + 9·875 = 14·74 ,, 14·8
4th ,, (15·10 − 10·15) × 1·0143 + 9·875 = 14·89 ,, 14·9
5th ,, (15·20 − 10·15) × 1·0143 + 9·875 = 14·99 ,, 15·0
24th ,, (15·55 − 10·15) × 1·0143 + 9·875 = 15·35 ,, 15·3
48th ,, (15·50 − 10·15) × 1·0143 + 9·875 = 15·30 ,, 15·3

Hence a limit value is reached within 24 hours of mixing, and neither oxidation of sulphurous acid nor formation of a polythionic acid has taken place. If either of the latter had occurred, the calculated iodine titration would have been greater than the observed value, which is not the case.

The change taking place in acidified solutions of sodium thiosulphate, where the products of the change are not eliminated from the system in which they are formed, having proved to be a reversible one, was investigated with a view to determine the effect of—

I. Variation in concentration.
II. Variation in the quantity of acid relative to the quantity of sodium thiosulphate.
III. Nature of the acidifying acid.
IV. Variation in the temperature at which the change proceeds.
V. The presence in the initial system of varying quantities of sulphurous acid.

The Effect of Concentration.

The solutions used in these experiments were made by diluting those employed in the last experiment to twice and four times their volumes. If the concentration of the solutions in the last experiment be taken as unity, the concentrations of the new solutions are $\frac{1}{2}$ and $\frac{1}{4}$. The iodine solution intended for the titration of the contents of the bulbs was also diluted to corresponding strengths.

The titrations of the sodium thiosulphate solutions in terms of iodine, gave that 10 c.c. of the solutions of concentrations 1, $\frac{1}{2}$, and $\frac{1}{4}$ required 19·85 c.c. of the iodine solutions of corresponding strengths. The acidifying acid solutions were proved to possess the relative concentrations 1, $\frac{1}{2}$, and $\frac{1}{4}$ by titrating them with one and the same ammonia solution. Moreover, the iodine solutions were shown to be in the ratio of $1 : \frac{1}{2} : \frac{1}{4}$ by their titrations with one and the same sodium thiosulphate solution.

The temperature of the bath for the three series of experiments was 30°.

Effect of concentration $t = 30°$. The solution of concentration 1 contains 4·885 grams $Na_2S_2O_3,5H_9O$ dissolved in 500 c.c. water. Each solution is acidified with the equivalent quantity of acid. 10 c.c. of each solution required, before acidification with an equal volume of the solution of the acid, 19·75 c.c. of an iodine solution of corresponding strength.

	Conc. 1.	Conc. $\frac{1}{2}$.	Conc. $\frac{1}{4}$.
Iodine titration at the end of the 1st hour	13·10	11·60	10·70
,, ,, ,, 2nd ,,	14·00	12·45	11·20
,, ,, ,, 3rd ,,	14·80	12·95	11·70
,, ,, ,, 4th ,,	14·90	13·15	12·00
,, ,, ,, 5th ,,	15·00	13·30	12·20
,, ,, ,, 48th ,,	15·30	14·25	13·20

These titrations give for the extent of chemical change as measured by the excess of the iodine titration over 19·75/2 = 9·9 (approx.).

	Conc. 1.	Conc. ½.	Conc. ¼.
At the end of the 1st hour	3·2	1·70	0·80
,, 2nd ,, ...	4·1	2·55	1·30
,, 3rd ,, ...	4·9	3·05	1·80
,, 4th ,, ...	5·0	3·25	2·10
,, 5th ,, ...	5·1	3·40	2·30
,, 48th ,, ...	5·4	4·35	3·30

The value 9·9 would represent complete resolution of thiosulphuric acid into sulphur and sulphurous acid.

Hence,

I. Increase in the concentration of the solution of sodium thiosulphate acidified with the equivalent quantity of hydrogen chloride is accompanied by increase in the rate and extent of the chemical change of thiosulphuric acid into sulphur and sulphurous acid.

II. With increase in concentration in the proportion 1 : 2 : 4, the values expressing the extent of chemical change in the first hour increase in the ratio $1 : 1 + a : 1 + 3a$, and the limit values in the ratio $1 : 1 + a : 1 + 2a$.

The actual change at the end of the 1st, 5th, and 48th hour corresponds to a percentage of the possible change is

	Conc. 1.	Conc. ½.	Conc. ¼.
At the end of the 1st hour..	32·3 p. c.	17·1 p. c.	8·08 p. c.
,, 5th ,, ..	51·5 ,,	34·3 ,,	23·2 ,,
,, 48th ,, ..	54·5 ,,	43·9 ,,	33·3 ,,

Effect of varying the Quantity of Acidifying Acid relatively to the Quantity of Sodium Thiosulphate.

These experiments were made with a sodium thiosulphate solution containing 4·885 grams of the crystallised salt dissolved in 500 c.c. of water. Solutions of hydrogen chloride of strengths ½, ¾, 1, 1¼, and 2 were used as acidifying acid, where concentration 1 contains the equivalent quantity of acid requisite for the saline decomposition, and 2 the double of that quantity. The titrations of these solutions of hydrogen chloride gave with one and the same ammonia solution—

10 c.c. of the acid of concentration	½.	¾.	1.	1¼.	2.
Required of ammonia solution.	10·05	15·15	20·25	25·35	40·40

10 c.c. of the solution of sodium thiosulphate required, previous to acidification, 19 c.c. of an iodine solution. This difference in the values of the sodium thiosulphate solutions in the last experiment and

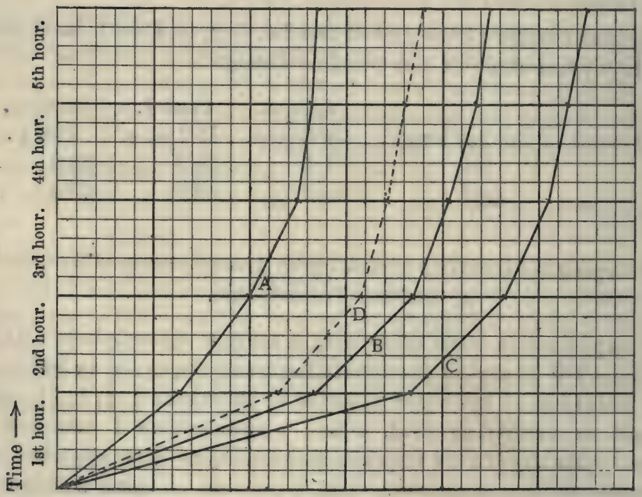
in the present one (19·00 instead of 19·75) is to be explained by the iodine solutions used in the two cases not being the same, and is not due to differences in concentration of the sodium thiosulphate solutions.

The temperature of the bath was 30°.

Effect of varying the quantity of acidifying acid relatively to the quantity of sodium thiosulphate, $t = 30°$. 10 c.c. of the sodium thiosulphate solution required 19 c.c. of the iodine solution. The acid of concentration 1 contained a quantity of acid sufficient for the saline decomposition—

With acid of concentration........	½.	¾.	1.	1¼.	2.
At the end of the 1st hour iodine titration gave	11·25	12·05	12·7	12·95	13·65
,, 2nd ,, ,,	12·00	12·90	13·7	13·90	14·65
,, 3rd ,, ,,	12·50	13·35	14·05	14·40	15·10
,, 4th ,, ,,	12·65	13·60	14·35	14·70	15·30
,, 5th ,, ,,	12·70	13·70	14·50	14·90	15·50
,, 48th ,, ,,	12·80	14·10	14·80	15·30	16·30

FIG. 2.



Chemical change → as measured by the excess of the titration over 10.

Quantity of acidifying acid relatively to the thiosulphate variable.

A. Quantity of acidifying acid half that requisite for complete saline decomposition.

B. Thiosulphate and acidifying acid in equivalent quantities.

C. Acidifying acid taken in quantities twice the equivalent.

D. H_2SO_4 used instead of 2HCl.

$t = 30°$ C.

The values expressing the extent of chemical change give—

With acid of concentration ...	½.	¾.	1.	1¼.	2.
At the end of the 1st hour ..	1·75	2·55	3·2	3·45	4·15
When the limit is reached ..	3·30	4·60	5·30	5·80	6·80
At the end of the 5th hour..	3·20	4·20	5·00	5·40	6·00

The value 9·5 would represent complete resolution of thiosulphuric acid into sulphur and sulphurous acid.

Hence—

I. Increase in the quantity of the acidifying acid relatively to the quantity of sodium thiosulphate produces an increase both in the rate and extent of the change of thiosulphuric acid into sulphurous acid and free sulphur.

II. This increase in the velocity and limit values does not cease when sufficient acid is present for complete saline decomposition, or, more correctly, when a quantity of acid is present which, in the case where the sulphurous acid formed by the decomposition of the thiosulphuric acid is eliminated from the system, suffices for complete saline decomposition.

III. As the quantity of acidifying acid relatively to the quantity of sodium thiosulphate increases, the effect of each successive equal increment in the strength of the acidifying acid produces a smaller increase in the velocity and limit values.

Effect of the Nature of the Acidifying Acid.

To ascertain whether or not the acidifying acid influenced the rate and extent of the chemical change, the following experiments were made, using hydrogen sulphate as acidifying acid. The solution of hydrogen sulphate was analysed gravimetrically and volumetrically with the following results :—

I. 30 c.c. gave 0·2796 gram $BaSO_4$.
II. 30 c.c. „ 0·2806 „ „
III. 10 c.c. required 10·1 c.c. of a solution of sodium carbonate containing 4·1760 grams of the pure dried salt in 1000 c.c. of its solution.

These results give that in 10 c.c. of the solution of hydrogen sulphate there is contained—

I. 0·0392 gram H_2SO_4. II. 0·0393 gram H_2SO_4.
III. 0·0389 gram H_2SO_4.

The quantity of hydrogen sulphate theoretically necessary for the complete saline decomposition of sodium thiosulphate containing

4·885 grams $Na_2S_2O_3,5H_2O$ in 500 c.c., assuming the decomposition to proceed according to the equation

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2S_2O_3,$$

is 0·0386 gram per 10 c.c.

First Series of Experiments (see Fig. 2, p. 188).—The solution of sodium thiosulphate contained 4·885 grams of the salt in 500 c.c., and 10 c.c. required 19 c.c. of the iodine solution employed. The temperature of the bath was 30°. The solutions of hydrogen sulphate and sodium thiosulphate were mixed in equal volumes.

Where the acidifying acid was	H_2SO_4.	HCl.
At the end of the 1st hour the iodine titration gave	12·30	12·70
„ 2nd „ „	13·15	13·70
„ 3rd „ „	13·40	14·05
„ 4th „ „	13·60	14·35
„ 5th „ „	13·80	14·50
„ 48th „ „	14·30	14·80

Second Series of Experiments.—The solutions of sodium thiosulphate and hydrogen sulphate used in the first series of these experiments were diluted to twice their volume. The temperature of the bath was 30°. The titration of the sodium thiosulphate in terms of the iodine solution used gave that 10 c.c. required 19·75 c.c. of the iodine solution.

Where the acidifying acid was	H_2SO_4.	HCl.
At the end of the 1st hour the iodine titration gave	11·45	11·60
„ 2nd „ „	12·05	12·45
„ 3rd „ „	12·45	12·95
„ 4th „ „	12·75	13·15
„ 5th „ „	12·95	13·30
„ 48th „ „	13·70	14·20

Third Series of Experiments.—The sodium thiosulphate solution was the same as that used in the second series. The hydrogen sulphate solution was of the same strength as that used in the first series. Hence, in this case there was sufficient hydrogen sulphate to effect the saline decomposition, supposing it to proceed according to the equation,

$$2H_2SO_4 + Na_2S_2O_3 = 2NaHSO_4 + H_2S_2O_3.$$

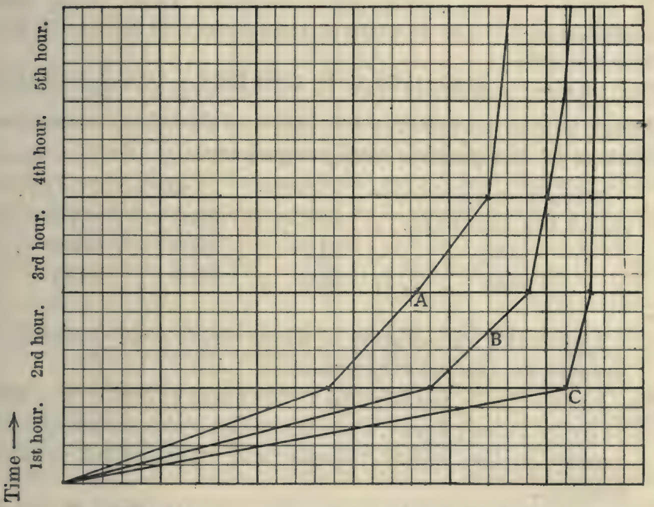
At the end of the......	1st hr.	2nd hr.	3rd hr.	4th hr.	5th hr.	48th hr.
The iodine titration gave	11·90	12·75	13·25	13·75	14·05	15·20 c.c.

Hence, where hydrogen sulphate and hydrogen chloride act upon the same quantity of sodium thiosulphate, in the proportions $H_2SO_4 : 2HCl$, the velocity and limit values are greater for hydrogen chloride. This result, too, is independent of the degree of concentration of the solution of sodium thiosulphate. Where, however, the masses of of the acidifying acid are in the proportion $2H_2SO_4 : 2HCl$, the velocity and limit values are greater for hydrogen sulphate.

Effect of Variation in the Temperature at which the Change proceeds.

In ascertaining the effect of varying this condition under which the change proceeds, the solution of sodium thiosulphate contained 4·885 grams of the crystallised salt per 500 c.c., and the solution of the acidifying acid a quantity of hydrogen chloride sufficient for the complete saline decomposition when equal volumes of the solutions were taken.

FIG. 3.



Chemical change ⟶ as measured by the excess of the titration over 10.

Temperature variable.

A = curve for system $Na_2S_2O_3 + 2HCl$. $t = 30°$ C.
B. $t = 40°$ C.
C. $t = 60°$ C.

The temperature of the bath was, in the three experiments, 30°, 40°, and 60°. In reality, the results already got for the temperature 30° were compared with those obtained for the new temperatures 40° and 60°.

10 c.c. of the sodium thiosulphate solution required 19·25 c.c. of the iodine solution used in the experiments at 40° and 60°.

10 c.c. of the hydrogen chloride solution required 19·70 c.c. of the ammonia solution used in the experiments at 40° and 60°.

The factor expressing the ratio of the iodine titration of sulphurous acid to the acidity of the solution after titration with iodine, in terms of these new solutions of iodine and ammonia equalled 15·3/15·05 = 1·016.

With the temperature of the bath at 40°—

At the end of the ..	1st hour.	2nd hour.	3rd hour.	4th hour.	5th hour.	24th hour.	96th hour.	96th hour.
The iodine titration gave	13·80	14·80	15·00	15·15	15·25	15·40	α, 14·90	β, 14·85
And the ammonia titration gave	14·00	15·00	15·20	15·30	15·40	15·60	α, 15·35	β, 15·30

With the temperature of the bath at 60°—

At the end of the...	1st hour.	2nd hour.	3rd hour.	4th hour.	5th hour.	24th hour.	24th hour.	Six days.
The iodine titration gave	15·20	15·45	15·45	15·50	15·50	α, 14·80	β, 14·75	11·70
And the ammonia titration gave...........	15·50	15·70	15·75	15·80	15·75	α, 15·45	β, 15·40	12·70

The change at the end of the 1st, 5th, and 24th hour corresponds to a percentage of the possible change equal to—

When the temperature =	30°.	40°.	60°.
At the end of the 1st hour....	32·3 p. c.	43·0 p. c.	57·5 p. c.
,, 5th ,, ...	51·5 ,,	58·0 ,,	60·6 ,,
,, 24th ,, ...	54·5 ,,	59·9 ,,	(?)

Hence—

I. The higher the temperature at which the change proceeds, the greater are the velocity values.

II. The limit value is not affected to the same extent as the initial velocity value; hence, the higher the temperature the more nearly do the initial velocity and limit values equal one another.

III. From the values for the system in which the change proceeds at the temperature 40°, four days after acidification, as well as from the values for the system in which the change proceeds at 60°, only 24 hours after mixing, it is evident some further change beyond the decomposition of thiosulphuric acid into sulphurous acid and sulphur has taken place, and that such change proceeds more readily at higher than at lower temperatures.

The Nature of the Secondary Change taking place in Acidified Solutions of Sodium Thiosulphate, where the Products of the Primary Change are not eliminated from the System in which they are formed.

When sodium thiosulphate is acidified with an equivalent quantity of acid, complete saline decomposition and complete decomposition of thiosulphuric acid into free sulphur and sulphurous acid ensue, provided the sulphurous acid so formed is eliminated from the system. Where, however, the sulphurous acid is retained in the system in which it is formed, the change of thiosulphuric acid into sulphurous acid and free sulphur proceeds with gradually diminishing velocity, until a limit is reached. At this point there is in the system thiosulphuric acid, protected from further change by the presence of the accumulated products of decomposition of thiosulphuric acid. In addition, there is, no doubt, some undecomposed sodium thiosulphate; for where there is in the system thiosulphuric acid, as well as the acidifying acid, there will be a division of the base between the acids, and some sodium thiosulphate will remain undecomposed, protected from change at the hands of the acidifying acid, by the thiosulphuric acid preserved in the system by the protective action of accumulated products of decomposition of thiosulphuric acid. The state of equilibrium, when this limit has been reached, will be overthrown if any secondary change between the products of the primary change, or between either of these products and unaltered hydrogen or sodium thiosulphate, supervenes; if the sulphurous acid and free sulphur react, and re-form thiosulphuric acid, or if the sulphurous acid and thiosulphuric acid interact and form a polythionic acid.

In the system $Na_2S_2O_3 + 2HCl$, in the case where the sodium thiosulphate solution containing 4·885 grams of the crystallised salt dissolved in 500 c.c. of water was acidified with the equivalent quantity of hydrogen chloride, and the temperature of the bath was 30°, the check on the iodine titration, which a determination of the acidity after titration with iodine gave, showed that no secondary change had taken place 48 hours after acidification (see p. 186).

The following experiments were made in order to ascertain whether or not, at a still later period from the time of acidification, this state of equilibrium attained within the first 48 hours was overthrown.

The solution of sodium thiosulphate contained 4·885 grams of the crystallised salt dissolved in 500 c.c. of its solution. It was acidified with hydrogen chloride in equivalent quantities.

10 c.c. of the thiosulphate of soda solution required, before acidification, 19·25 c.c. of the iodine solution.

10 c.c. of the hydrogen chloride solution, before being mixed with an equal volume of the thiosulphate of soda solution, required 19·70 c.c. of the ammonia solution.

The factor expressing the ratio $\frac{\text{iodine titration}}{\text{acidity after titrating with iodine}}$ $= \frac{15·25}{15·00} = 1·016.$

The temperature of the bath was 30°.

At the end of 24 hours, the iodine titration gave 15·15, and the ammonia 15·35.

	The iodine titration gave	And the ammonia titration gave
At the end of 48 hours	(1) 15·20	(1) 15·40
,, ,, ...	(2) 15·15	(2) 15·40
,, ,, ...	(3) 15·15	(3) 15·35
At the end of 96 hours	(1) 14·80	(1) 15·25
,, ,, ...	(2) 14·90	(2) 15·35
At the end of 9 days	14·55	15·10
,, 16 ,, ...	14·00	14·65
At the end of about 2 months	12·35	13·20

Some bulbs were charged with sulphurous acid and placed in the bath, where they were kept for different lengths of time.

10 c.c. of the sulphurous acid solution required 15·25 c.c. of the iodine solution, and, after titration with iodine, 15·00 c.c. of the ammonia solution.

At the end of 48 hours, the sulphurous acid contained in a bulb required 15·25 c.c. iodine and 15·00 c.c. ammonia solution.

At the end of 6 days, the sulphurous acid contained in a bulb required 15·25 c.c. iodine.

At the end of 16 days, the sulphurous acid contained in a bulb required 15·15 c.c. iodine.

Hence, the reason for the diminution in the iodine titration of the contents of the bulbs is not to be explained by oxidation of a part of the sulphurous acid. Nor can it be explained by supposing that reformation of thiosulphuric acid, by the interaction of sulphurous acid and free sulphur, ensues; for in that case the same ratio between the excess of the iodine titration over the initial titration, to the excess of the acidity titration after addition of iodine over the initial acidity titration, would be maintained. That this is not the case is readily seen from the following values:—

The value of the ratio $\dfrac{\text{excess iodine over initial iodine titration}}{\text{excess over initial acidity of acidity after iodine titration}}$

At the end of 48 hours ...... = 1·001
,, 96 ,, ... = 0·958
,, 9 days........ = 0·938
,, 16 ,, ... = 0·911
,, 2 months ..... = 0·813

Hence there is, as the iodine titration gradually diminishes, a gradual diminution in the above ratio, and therefore the formation of an acid which does not possess an iodine titration, or an acid which, compared with its equivalent in acidity in thiosulphuric acid, possesses a smaller iodine titration.

By similarly considering the results obtained for the same system, but at the temperatures 40° and 60°, it is seen that this same secondary change is proceeding, but with much greater velocity.

When the temperature of the bath equals 40°—

The value of the above ratio after 24 hours = 1·003
,, ,, ,, 96 ,, = 0·958

When the temperature of the bath is 60°—

The value of the above ratio after 5 hours = 0·996
,, ,, ,, 24 ,, = 0·906
,, ,, ,, 6 days = 0·728

At the end of 12 days, the iodine titration had sunk below its initial value, but the acidity was in excess of its initial value. The titrations gave, iodine titration = 9·45 c.c.; ammonia titration = 10·85 c.c. Hence—

I. The method of investigation shows that after the lapse of a certain period from the time of acidification, the sulphurous acid reacts with either sodium or hydrogen thiosulphate, and forms an acid possessing either no iodine titration, or a less one than that of its equivalent in acidity of thiosulphuric acid.

Such a change might proceed according to the equations

$$2Na_2S_2O_3 + 3SO_2 = 2Na_2S_3O_6 + S,$$

or,

$$2H_2S_2O_3 + 3SO_2 = 2H_2S_3O_6 + 3.$$

II. This secondary change proceeds more rapidly the higher the temperature, and with the higher temperature the time elapsing between the acidification of the sodium thiosulphate and the secondary change becoming apparent diminishes.

Debus, in his paper on the "Chemical Investigation of Wackenroder's Solution" (Trans., 1888, **53**, 343), states that sulphurous acid reacting with potassium thiosulphate forms potassium trithionate, and the salt so formed takes up the sulphur set free during the interaction of sulphurous acid and potassium thiosulphate, yielding potassium tetrathionate and pentathionate. In the same paper, he shows that sulphurous acid, by its action on potassium pentathionate, gives potassium trithionate and thiosulphuric acid. Pentathionic acid, or a pentathionate, gives with an ammoniacal solution of silver nitrate a white precipitate, which gradually darkens in colour. This is a reaction characteristic of pentathionic acid, and not given by trithionic acid or tetrathionic acid.

The contents of a bulb which had been kept so long in the bath that the secondary change had proceeded to a considerable extent were tested with an ammoniacal solution of silver nitrate, but no precipitate was formed. Hence, pentathionic acid was not formed in the secondary change.

Effect of the Presence in the Initial System of Varying Quantities of Sulphurous Acid.

The solution of sodium thiosulphate contained 4·885 grams of the crystallised salt dissolved in 500 c.c. of water. The solution of the acidifying acid contained of hydrogen chloride per c.c. the double of the quantity requisite for the saline decomposition of the sodium thiosulphate contained in an equal volume of its solution. A certain volume of a solution of sulphurous acid, whose titration in terms of the iodine solution had been previously ascertained, was added to an equal volume of the acidifying acid solution, and this mixed solution was diluted to twice its volume by the addition of an equal volume of the solution of sodium thiosulphate. Thus the acidifying acid and sodium thiosulphate were taken in equivalent quantities, and the sulphurous acid present in any volume of the acidified thiosulphate solution was one fourth of the quantity in the original solution of sulphurous acid whose iodine titration had been determined.

The temperature of the bath was 30°. 10 c.c. of the solution of sodium thiosulphate required 19·90 c.c. of the iodine solution used.

First Series of Experiments.—10 c.c. of the sulphurous acid required 8·6 c.c. of the iodine solution.

This solution of sulphurous acid was prepared by passing a stream of hydrogen through a concentrated solution of sulphur dioxide in water, and dissolving the sulphur dioxide so displaced, in boiled distilled water which had been cooled in a stream of hydrogen.

At the end of the	1st hour.	2nd hour.	3rd hour.	4th hour.	5th hour.	48th hour.
The iodine titration gave	14·85	15·65	16·05	16·20	16·45	17·05
Or subtracting the iodine titration of the sulphurous acid originally added $= \frac{8·6}{4} = 2·15$	12·70	13·50	13·90	14·15	14·30	14·90

Second Series of Experiments.—10 c.c. of the sulphurous acid solution required 45 c.c. of the iodine solution; $\frac{45}{4} = 11·25$ = the titration in terms of iodine of the sulphurous acid initially in the bulb.

At the end of the	1st hour.	2nd hour.	3rd hour.	4th hour.	5th hour.	48th hour.
The iodine titration − 11·25 gave..	12·30	13·15	13·45	13·75	13·90	14·15

These values are less than those on p. 185, and seem to point to a diminished velocity and limit value by reason of the sulphurous acid initially present. However, a determination of the acidity values showed this diminution in iodine titration to be accompanied by an increase in the acidity after titration with iodine, beyond the value calculated for this quantity from the iodine titration. Moreover, as the time from acidification becomes greater, there is a gradual increase in this excess of the acidity after titration with iodine over the calculated value, but it does not, except in the case of the limit value, account for the whole of the diminution in iodine titration.

Hence, from these results, sulphurous acid seemingly does slightly diminish the velocity and limit values. Such diminution is in part due to an interaction between sulphurous acid and sodium or hydrogen thiosulphate.

The diminution in the limit value in the case of the second series of experiments is entirely due to the interaction of sulphurous acid and sodium or hydrogen thiosulphate.

With a quantity of sulphurous acid initially present, approximately equally to the quantity of sulphurous acid in the system when the limit values (p. 185, *e.g.*) are obtained, the diminution in velocity values is very small, and with limit values probably *nil*.

General Conclusions which the Work leads to.

The decomposition of thiosulphuric acid into sulphurous acid and free sulphur proceeding in an acidified solution of sodium thiosulphate reaches a limit short of complete decomposition in the case where the products of the change are retained in the system in which they are formed. On the other hand, where sulphurous acid resulting from the decomposition of thiosulphuric acid is eliminated from the system, sodium thiosulphate acidified with an equivalent quantity of acid suffers complete resolution into sulphurous acid and free sulphur. It must, however, be concluded from the experiments, in which the effect of the presence in the initial system of varying quantities of sulphurous acid is determined, that sulphur and sulphurous acid, and not sulphurous acid alone, are instrumental in bringing about this state of equilibrium short of complete decomposition. For a quantity of sulphurous acid initially present, slightly greater than the quantity of sulphurous acid present, when the limit value is reached in the same system in the case where no sulphurous acid is initially present, produces but a very small diminution in velocity values, and probably no effect on the limit value. The attainment of this limit value is due to the retention in the system of the products of the decomposition of thiosulphuric acid, namely, sulphurous acid and free sulphur. There is in the system in this state of equilibrium, thiosulphuric acid, protected from further change by the accumulated products of the decomposition of thiosulphuric acid, sodium thiosulphate, protected from saline decomposition at the hands of the acidifying acid by the presence of thiosulphuric acid, the products of decomposition of thiosulphuric acid, and some small remnant of the acidifying acid. The effect on the velocity and limit values of varying the conditions under which the change proceeds has, in the course of the work, been investigated, and the results, when summarised, show—

1. With stronger solutions, the decomposition of thiosulphuric acid proceeds further before a limit is obtained.

2. Increase in the quantity of the acidifying acid relatively to the sodium thiosulphate increases the velocity and limit values. If we suppose that by the preservation of thiosulphuric acid in the system the basic radical (sodium) divides itself between the acidifying acid and thiosulphuric acid, increase in the mass of acidifying acid must produce increased saline decomposition and so overthrow the balance.

3. The same considerations explain how the nature of the acidifying acid can affect the velocity and limit values. It was found that 2HCl produces a greater resolution of thiosulphuric acid into sulphurous acid and free sulphur than H_2SO_4.

4. The velocity and limit values are affected by the temperature at which the change proceeds, the latter to a less degree than the former. At higher temperatures, the interaction of sulphurous acid and sodium or hydrogen thiosulphate proceeds more rapidly and further.

5. The presence of sulphurous acid in the system before acidification, retards slightly the velocity values. At the same time, an interaction between the sulphurous acid and sodium or hydrogen thiosulphate proceeds.

As regards the secondary change which is regarded as the formation of a polythionic acid by interaction of sulphurous acid and hydrogen or sodium thiosulphate, it may proceed from the moment of acidification simultaneously with the direct change, but its extent must be very small, not to be revealed by the experimental method followed, namely, the determination of the acidity of the solution after the iodine titration has been made. Pentathionic acid was not found as one of the products of this secondary change.

The addition of iodine to a mixed solution of sodium sulphite and sodium thiosulphate does not produce a trace of sodium trithionate. Hence, Spring's statement is not true of the case where a solution of iodine reacts with a mixed solution of sodium sulphite and thiosulphate.

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XIV.—*Action of Sulphurous Acid on Flowers of Sulphur.*

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Flückiger found that by the action of sulphurous acid on flowers of sulphur, traces of thiosulphuric acid were formed. The reaction proceeded more easily if the temperature was maintained between 80° and 90° (*Jahresbericht*, 1863, 149).

Debus (Trans., 1888, **53**, 347) says: "The two tubes" (one containing 36 c.c. of a concentrated solution of sulphurous acid and 10 grams of sulphur, and the second the same volume of sulphurous acid without any sulphur) "remained for five days at common temperatures, and were then heated for several hours on a water-bath to 60—80°. This treatment did not appear to have effected any change in either of the tubes. Both were now opened, their contents transferred to evaporating dishes, and warmed on water-baths until all the sulphurous acid had volatilised. Both liquids were finally concentrated to one-fifth of their original volume."

Proceeding in this way, Debus found that the only product of the action of sulphur and sulphurous acid was an infinitesimal quantity of pentathionic acid, and that its presence was revealed only by one test, and this he regarded as insufficient to allow of the conclusion that pentathionic acid had been formed by the interaction of sulphurous acid and flowers of sulphur.

Quantities of from 3 to 5 grams of flowers of sulphur, which had been washed first with warm, then with cold water, until the washings were no longer acid and possessed no iodine titration, were introduced into glass tubes, sealed at one end. After partly drawing out the other ends of the tubes, and displacing the air by carbon dioxide, 30 c.c. of a solution of sulphur dioxide in boiled water were added to each tube. Equal volumes of the same solution of sulphurous acid were introduced into other tubes containing no sulphur, and served as standards of the strength of the sulphurous acid solution.

First Series of Experiments.—Four tubes were so charged with sulphurous acid and flowers of sulphur; two with sulphurous acid alone. The six tubes, sealed before the blowpipe, were placed in an air-bath and heated at 85° for six days. Their contents were then rinsed into flasks, and their iodine titrations determined.

The tubes containing sulphurous acid alone required—

I. 61·70 c.c. of the iodine solution.
II. 62·50 " " "

The tubes containing sulphur and sulphurous acid required—

I. 32·25 c.c. of the iodine solution.
II. 32·85 " " "
III. 35·40 " " "
IV. 31·70 " " "

No. III contained only a very small quantity of sulphur, about 0·5 gram.

Hence the sulphurous acid has acted upon the sulphur, and has undergone a corresponding diminution in its iodine titration.

Second Series of Experiments.—In this second series of experiments, the attempt was made to ascertain the nature of the product or products of the action of sulphurous acid on sulphur. The development of acidity after titration with iodine was used to determine what part of the titration value in terms of iodine was due to sulphurous acid still present.

10 c.c. of a solution of sulphurous acid, carefully prepared so as to be free from sulphuric acid, by dissolving in boiled water, sulphur dioxide displaced from its aqueous solution by a stream of hydrogen gas, required—

5·5 c.c. of an ammonia solution to neutralise it.

The neutralised solution required—

20·95 c.c. of an iodine solution.

The developed acidity required—

15·60 c.c. of an ammonia solution to neutralise it.

Hence, (1) The developed acidity titration $\times \frac{20·95}{15·60} = 1·34$

gives the iodine titration of the sulphurous acid.

(2) The developed acidity titration $\times \frac{5·50}{15·60} = 0·35$

gives the acidity titration of the sulphurous acid in terms of the iodine and ammonia solutions used.

Methyl-orange was used as an acidity indicator, and starch with the iodine titrations. The blue colour of the starch iodide was discharged by a drop of sodium thiosulphate before the determination of the developed acidity.

A number of tubes, prepared exactly as in the first series of experiments, were treated in different ways, and their contents titrated with the ammonia and iodine solutions. In ascertaining the end of the acidity titrations, it was found advisable to withdraw portions of the almost neutralised liquid into a clean flask. In the absence of sulphur, the end of these acidity reactions was so much more easily recognisable.

No. I contained 2 grams of sulphur, and, after standing at the ordinary temperature of the air for two months, was heated for a week to a temperature of from 80—90°.

Initial acidity titration ... = 15·8
Iodine titration.......... = 21·55
Developed acidity titration = 14·80.

14·80 × 0·35 = 5·2.
14·80 × 1·34 = 21·85.

1·75 c.c. iodine due to thiosulphuric acid.

No. II contained 3 grams of sulphur, and was treated exactly as No. I.

Initial acidity titration ... = 15·70
Iodine titration.......... = 24·85
Developed acidity titration = 16·30.

16·30 × 0·35 = 5·70.
16·30 × 1·34 = 21·85.

3·00 c.c. iodine due to thiosulphuric acid.

No. III contained 5 grams of sulphur, and, after standing at the temperature of the air for two months, was heated for a week at 80—90°, and then allowed to stand another month at the air temperature.

Initial acidity titration ... = 15·5
Iodine titration.......... = 23·1
Developed acidity titration = 14·7.

14·7 × 0·35 = 5·15.
14·7 × 1·34 = 19·7.

3·4 c.c. iodine due to thiosulphuric acid.

No. IV contained 3 grams of sulphur, and, after standing for two months at the temperature of the air, was titrated. It was not heated.

Initial acidity titration ... = 14·5
Iodine titration.......... = 38·2
Developed acidity titration = 27·7.

27·7 × 0·35 = 9·7.
27·7 × 1·34 = 37·1.

1·1 c.c. iodine due to thiosulphuric acid.

Two tubes containing sulphur and distilled water, one of which, after standing for the two months at the air temperature, was heated to 80—90°, and the other merely kept at the temperature of the air for the two months, were examined. In neither case was there anything acidic or possessing an iodine titration formed.

The mean of three titrations of the sulphurous acid solution, made at the time of sealing the tubes, gave:—

30 c.c. (the volume introduced into each of the tubes) required 48·3 c.c. of the iodine solution.

This gives for the initial acidity titration a value 12·6 c.c. of the ammonia solution.

This gives for the developed acidity titration a value 36·05 of the ammonia solution.

In considering the interpretations which the above results bear, it must be noticed—

I. That sulphurous acid titrated with ammonia, using methyl-orange as an indicator, shows neutrality when the point corresponding to the formation of $NH_4{\cdot}HSO_3$ has been but slightly overstepped.

II. That where sulphurous acid oxidises to sulphuric acid, there is almost a doubling in the initial acidity value, and a complete loss of iodine titration, and of developed acidity.

III. That where sulphurous acid unites with sulphur there will be, if thiosulphuric acid is formed, almost a doubling of the initial acidity value, a halving of the iodine titration value, for

$$H_2SO_3 + I_2 + H_2O = 2HI + H_2SO_4,$$

but

$$2H_2S_2O_3 + I_2 = 2HI + H_2S_4O_6.$$

IV. That supposing the two equations

$$H_2SO_3 + S = H_2S_2O_3,$$
$$2H_2S_2O_3 + 3H_2SO_3 = 2H_2S_3O_6 + 3H_2O + S$$

to represent the change taking place when sulphur and sulphurous acid interact, the initial acidity will be approximately $\frac{4}{5}$ of its original value, if all the sulphurous acid becomes converted into trithionic acid. Further, as sulphurous acid becomes converted into trithionic acid, its iodine titration and developed acidity titration are completely lost.

V. That anything possessing an iodine titration, which is not sulphurous acid, may be thiosulphuric acid.

VI. That the initial acidity titration of sulphurous acid is about $\frac{1}{4}$ of its iodine titration in terms of the ammonia and iodine solutions used.

From the results of the titrations given above, the following conclusions may be drawn :—

1. That sulphur and sulphurous acid do react even at the ordinary temperature of the air. The action in this case is slow, but a temperature of from 80—90° greatly accelerates it.

2. There is in the solution a small quantity of something possessing an iodine titration, which is over and above the iodine titration of the still unaltered sulphurous acid. This may be thiosulphuric acid.

3. The initial acidity titration shows that there is present a quantity of something possessing an acidity, but no iodine titration. Some small part of this is, undoubtedly, oxidised sulphurous acid; but the greater part cannot be sulphuric acid, because, in that case, the initial acidity titration would be greater than 12·6 (the initial acidity value of the standard) by one-fourth of the diminution in the iodine titration. The increase in initial acidity titration due to thiosulphuric acid is approximately half the diminution in iodine titration consequent on its formation. There is present in the system something acidic, and without iodine titration. This may be a polythionic acid, trithionic, tetrathionic, or pentathionic acid.

The following qualitative tests were made with the contents of the tubes which had been, in the case of the first, allowed to stand the two months, then heated at 80—90°; in the case of the second, allowed to stand at the temperature of the air for two months; in the case of the third, kept in the dark at the temperature of the air for three months.

First Case. The tube had been heated at 80—90°.—Mercurous nitrate gave an instantaneous black precipitate (sulphurous acid will also give this). Silver nitrate produced a yellow precipitate, which very rapidly blackened on gently warming. Ammoniacal silver nitrate, in presence of excess of ammonia, did not give a precipitate. Cupric sulphate gave, on boiling, black copper sulphide.

Second Case. The tube had not been heated.—Silver nitrate gave a yellow precipitate, changing to black, even with a portion of the liquid from which sulphurous acid had been boiled off. Copper sulphate gave, on boiling, black copper sulphide. Ammoniacal silver nitrate produced no precipitate.

Third Case. The tube had been kept in the dark, wrapped in black paper, for three months.—Silver nitrate gave a white, changing to yellow and red, precipitate, which, on gently warming, became black. Ammoniacal silver nitrate produced no precipitate. Copper sulphate, on boiling, gave copper sulphide.

These qualitative tests point to the presence of thiosulphuric acid, trithionic acid, tetrathionic acid, or a mixture of any two or all three of these acids. Pentathionic is not present because of the absence of a precipitate with ammoniacal silver nitrate. Further, the precipitates were less bulky in the last two cases than in the first case.

Conclusions.

1. Sulphurous acid does react with flowers of sulphur, even in the dark, at the ordinary temperature of the air. With a higher temperature, the reaction proceeds still further, and there is formed, in addition to thiosulphuric acid, trithionic or tetrathionic acid, or both.
2. Pentathionic acid could not be detected by the ammoniacal silver nitrate test.

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XV.—*The Structure and Chemistry of Flames.*

By Arthur Smithells, B.Sc., and Harry Ingle, B.Sc., 1851 Exhibition Science Scholar (1891), the Yorkshire College, Leeds.

During the past 12 months we have been engaged in investigating some new points in connection with the structure and chemistry of flames. The investigation, which at first proceeded rapidly, has latterly become more complex and difficult, and much more work is demanded for the complete solution of the problems that have arisen. We fully intended to delay the publication of our results until material for a complete memoir had been accumulated, especially as we believed ourselves to be working in an obscure corner of the subject. But in the *Journal für praktische Chemie*, **44**, 246, there appeared a paper "Zur Kennzeichnung der Flamme," by N. Teclu, which was first brought to our notice by an abstract in this Journal (1891, 1309), and the paper gives a description of the very phenomenon which served as the starting point of our experiments. The author also, in a footnote, reserves to himself the investigation of the field to which this phenomenon opens the way. As the phenomenon in question was observed by one of us three or four years ago, and has indeed been since shown as a lecture experiment, and as we have been so long engaged in working out the points suggested by it, we feel compelled to give an account of our experiments as far as they have gone, and to indicate the directions in which we propose to extend them. The greater part of the account which follows was, we may say, in manuscript before Herr Teclu's paper came under our notice.

The experiments to be described were undertaken with the general object of enquiring into the structure of hydrocarbon flames. By employing hydrocarbons of definite composition we hoped that it would be possible to trace the chemical changes taking place in different regions of the flame with more accuracy and definiteness than is possible with coal-gas, paraffin, or other mixtures such as have been used by previous investigators.

By something of the nature of an accident, the enquiry has been directed in the first instance to the study of non-luminous flames. A long, glass tube was fixed over a Bunsen burner so as to form practically a wider prolongation of the metal tube, and the ordinary non-luminous flame was obtained at the top of it. On diminishing the supply of gas or increasing the supply of air, such a flame assumes the well-known, clearly-defined, two-coned structure, the inner cone becoming gradually flatter and smaller, more sharply defined, and distinctly green in colour. If the gas supply be further diminished, the flame eventually passes down the glass tube, until after a period of rapid vibration it either causes the detonation of the mixture in the tube and lights the gas at the bottom, or else it goes out.

This experiment has been shown by Professor H. B. Dixon to illustrate the initiation of the explosive wave, and the phenomena observed are similar to those photographed and described by Mallard and Le Chatelier in their experiments on the same subject (*Bull. Soc. Chim.*, **39**, 572; Abstr., 1884, 46, 549).

An attempt was made to cause the retreating flame to register its course by coating the interior of the tube thinly with wax, and some interesting markings were obtained. We hold this matter in reserve for the time being.

On carefully regulating the supply of gas and air so that the flame would just, but only just, recede, it was found that the flame would pass down the tube for 12 inches or so, and then return to the top; and in this way an oscillation of the flame could be maintained for some minutes. On carefully inspecting the apparatus when in this condition, it was found that the flame did not recede as a whole, but that, in fact, it split into two parts (i), an inner cone which became flatter and greener as it entered the tube and descended the latter like a piston with a convex under surface, and (ii), a larger, scarcely-luminous, lilac-coloured cone which remained in its original position at the top of the tube. It was obvious that this division of the flame corresponded to the two-coned structure of a Bunsen flame, and the experiment made it clear that in a Bunsen flame we have two distinct stages and areas of combustion defined respectively by the inner and outer cones of flame. The apparatus seemed to promise a means of widely separating these regions and of examining the gases between them without any possibility of diffusion of the outside air or of gases from other parts of the flame. For this purpose, it was necessary to devise some means whereby, after the flame had been divided into two cones, these could be kept separate whilst some of the gases from the interconal space was aspirated for analysis.

It will perhaps be well at this point to consider the reason for the division of the flame. When a Bunsen flame is burning at the top of a tube in the ordinary way, the coal-gas is in such excess that the mixture within the tube is scarcely explosive. If now the proportion of coal-gas to air be diminished, the mixture within the tube becomes more explosive, and the initial velocity of inflammation of this mixture increases as the proportion of air is increased up to a certain point. Long before enough oxygen is mixed with the gas for its complete combustion, the explosibility of the mixture has reached such a point that the velocity of inflammation is greater than the velocity of efflux from the tube, and so the flame is differentiated into two cones, one of which descends the tube and marks the margin of the explosive mixture. The other cone marks the area of combustion of the combustible gases which have escaped combustion in the lower cone, and are burning at the top of the tube in free air. Now the rate at which the inner cone will continue to descend the tube will depend upon several conditions, one of which is the temperature, another the diameter of the tube, and these considerations suggested a means of arresting the lower cone of flame. By heating the glass tube with a blowpipe flame at a point about a foot below the top, it was found possible to arrest the inner cone when *reascending;* the high temperature producing locally a velocity of inflammation greater than that at points above or below, and so fixing the flame. The second method suggested by the foregoing considerations was simply to diminish the diameter of the tube at one point either by means of a metal diaphragm or by slightly drawing out the tube so as to cause a constriction. At the narrow part of the tube, the velocity of the ascending gas mixture is obviously greater than elsewhere, and hence a flame which will descend the wider part of the tube will be arrested at this point. With this apparatus, the flame could be divided with the greatest ease, and the two regions of combustion kept separate for any length of time.

The apparatus finally adopted was constructed as shown in Fig. 1. A Bunsen burner A is fitted to a glass tube BC by means of a perforated cork or a packing of cotton wool. The upper part of this tube is sheathed with a wider one EF, and connected to it by a joint at E.

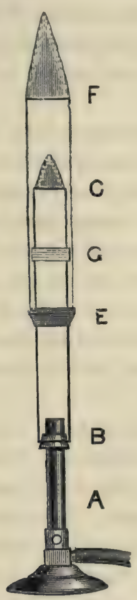

FIG. 1.

The most suitable joint for this purpose is an india-rubber tobacco-pipe cover, the flat disc of which can be punched out with a cork-borer so as to admit the inner tube. Whilst maintaining an air-tight connection, this admits of the free up and down movement of the inner tube.

The two tubes are kept coaxial by a ring of asbestos at G. Rings of brass foil may be fitted into the ends C and F of the glass tubes to diminish the risk of cracking by heat, and to avoid coloration of the flame by the sodium of the glass.

If the apparatus be arranged so that the mouth of the inner tube is about 10 cm. below that of the outer one, and the gas be lighted, an ordinary Bunsen flame is obtained at the mouth of the latter. If now the gas supply be gradually diminished, the flame becomes smaller, and the two-coned structure more evident until the inner cone, having become very small and green in colour, shows a tendency to enter the tube. As the gas supply is further cut off, the inner cone will probably descend and reascend a few centimetres, until finally it descends as far as the orifice of the inner tube at C, on which it will then suddenly settle and remain. This point is equivalent to a constriction in the tube, and the consequent increase in the velocity of ascending gases determines the sudden arrest of the receding flame. Whilst this is going on, a feeble flame consisting of a single hollow cone of pale lilac colour remains at the orifice of the outer tube F. The two conical areas are thus widely separated, and the gases coming from the lower one can be easily aspirated by introducing one limb of a bent tube at F.

That these two cones correspond to the two cones of a Bunsen flame is evident from the course of the experiment, but it may be seen still more plainly by modifying the procedure as follows:—The apparatus is arranged so that the inner tube projects above the outer one, and the Bunsen flame is obtained on the former. The gas supply is then cut off till the inner cone is on the point of descending, but is still burning steadily. The outer tube is then slid slowly up beyond the inner tube, and it will be seen to cleanly detach and carry up the outer cone from the inner one, which remains in its original position at the top of the inner tube.

An idea of the distribution of heat may be obtained by stretching an iron wire along the axis of the two tubes, when it will be seen that the brightest glow is where the wire passes through the top of the lower cone. Below and above this point the wire remains dark until it passes through the tip of the upper cone. It is evident that both cones are hollow, and that the lower one is much the hotter. Its temperature appears to lie between the melting point of copper and iron, that is, above 1300°.*

Instead of using the apparatus as shown in Fig. 1 (the handiest form for a lecture experiment), it has been found more convenient to dispense with the Bunsen burner, and to have the supplies of gas and air under complete control; and to this end the gases have been forced in from gas-holders through a ┬-piece passing through a cork at B. This arrangement also allows the experiment to be carried a stage further. If, after the air and gas have been adjusted so as to produce a separation of the cones as above described, the supply of air be further increased, the explosibility of the mixture increases, the inner cone darts down, the upper one disappears, and the combustion goes on at B, where the gases enter the apparatus. On further increasing the air-supply, the flame goes out, but a little more air now *diminishes* the explosibility of the mixture, and it is found possible to ignite it when it burns in a simple cone at C. This is a flame burning with excess of air, and, being no longer a seat of

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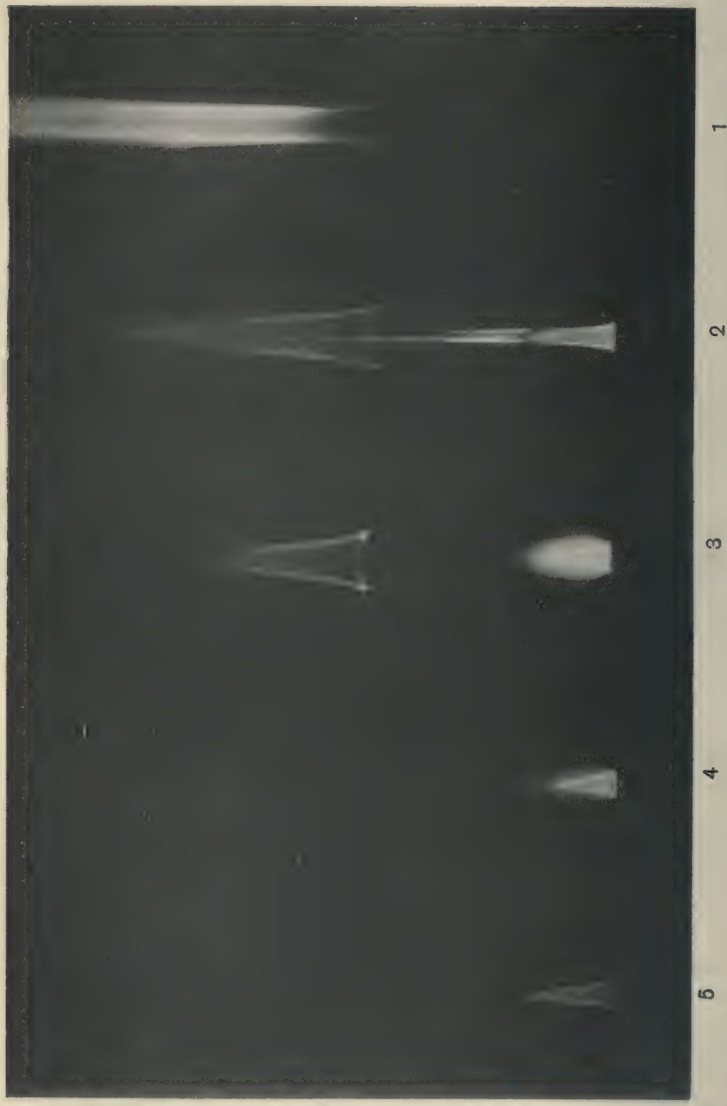
* Rosetti (*Ber.*, 1877, 2054, and 1878, 809) gives the temperature of the inner cone of an ordinary Bunsen burner as below 1200°, and the highest temperature outside it as 1360°. According to Bunsen ("Flammenreactionen") the highest temperature is midway between the tip of the inner cone and the nearest point of the outer one.

Journ. Chem. Soc. March, 1892. PLATE I.



partial combustion, is indivisible. More air merely cools it, until finally it goes out. We thus pass from a Bunsen flame in which there are excess of coal-gas and two areas of combustion to a flame where there is excess of air and only one cone of combustion.

To use the apparatus for non-luminous flames from liquid hydrocarbons, all that is required is a current of air from a gas-holder, so arranged that any desired fraction can be sent through a "saturator." Such saturators as are used for the ether-oxygen lime-light serve excellently; but for ordinary purposes a wide glass tube, containing a roll of flannel soaked with the hydrocarbon, answers very well. The air, after passing through the saturator, rejoins the main current, and passes into the apparatus, where, by suitable regulation, a non-luminous flame can be obtained, and separated into two cones. The appearances presented are, in the case of liquid hydrocarbons, not quite the same as with those which are ordinarily gaseous. As a rule, with the vapours of liquid hydrocarbons a considerable degree of luminosity is maintained until the moment of descent of the inner cone, whereupon both cones become non-luminous. Besides this, the inner cone presents a peculiar appearance. It is divided by dark lines into several (usually five or six) petal-like segments, which often revolve with great rapidity round a vertical axis. Air charged with benzene vapour affords an example of this class of flames, and with it also two more points of special interest may be observed. If, after the two non-luminous cones have been separated, the supply of benzene-vapour be increased, a luminous tip appears in the inner cone, and on further increasing the benzene this tip extends as a vertical streak of separated carbon. It is luminous for some distance above the inner cone, then cools down, and only becomes incandescent again on passing through the tip of the upper cone. If the benzene supply be diminished, the luminous streak disappears, the upper cone becomes smaller and smaller, and finally disappears altogether. Meanwhile, the inner cone has become smaller, and more vividly blue and hotter, and now the whole combustion is taking place in this single cone of flame. If more benzene be cut off, the proportion of air becomes excessive, the flame cools, loses brilliance, and slightly enlarges. Finally, a further diminution of benzene caused the flame to rise from the inner tube, slowly pass upwards, and disappear. These appearances are shown in Plate I, which is from photographs, and represents the gradual transition without even momentary extinction from a flame containing excess of hydrocarbon to one containing excess of air.

Analytical Methods.—The first analyses, made with a view to determining approximately the constituents of gases coming from the inner cone of flame, were done with Hempel's apparatus. The apparatus subsequently employed was of two kinds, one for gravimetric determinations specially devised, and the other the gas analysis apparatus invented by Dittmar and Lennox, and constructed for us by Messrs. Baird and Tatlock. We do not propose at present to describe either apparatus. A description of the Dittmar-Lennox apparatus in its present form has not yet been published, but the essential features are described by Professor Dittmar, in the new edition of *Watts's Dictionary of Chemistry*, **1**, 245. We have to express our indebtedness to Mr. Lennox, for valuable assistance in connection with the use of the apparatus, which we have found exceedingly handy. The volumetric process is of course much the shorter and easier, but the quantity of gas used is small, and we were driven to use a gravimetric method, in order to have a means of directly determining water-vapour, and, by operating on large quantities of gas, to have a control for the volumetric process more usually employed.

It is unnecessary here to enter into details of the methods of carrying out the analysis and calculating results. We have made many dozens of analyses, and, knowing to what extent the methods are trustworthy, shall be careful to give only such results as we believe to be quite reliable for the purposes for which they are used. We take this course chiefly because it now appears to us necessary to devise still more accurate methods for dealing with the problems raised by our experiments, and we hope eventually to repeat all our analyses with a new apparatus. The methods used break down when small quantities of hydrocarbons have to be determined.

Experiments with Hydrocarbons.

We proceed to give a list of the hydrocarbons used, adding remarks as to any special features noticed.

Ethylene.—The two cones may be separated before the lower one is free from separated carbon, or they may be made non-luminous. In the former case some acetylene comes from the inner cone.

Methane.—Both cones non-luminous.

Pentane.—Inner cone channelled by dark spaces, and open at the tip.

Heptane.—Same as pentane.

Benzene.—Already described. The inner tube must have a smaller diameter than in the other cases, otherwise it is impossible to arrest the inner cone. When the inner cone has a luminous tip, it gives off acetylene.

Coal-gas.—Already described. Tubes of various diameters were used.

The following numbers are extracted from our experimental results, and in most cases were repeatedly verified.

Gas.	C_2H_4.	C_2H_4.	CH_4.	C_5H_{12}.	C_7H_{16}.	C_6H_6.	Coal gas.		
Diameter of outer tube in mm. . . .	29	29	29	20	20	19	29	19·5	28
Diameter of inner tube in mm. . . .	20	20	20	13	13	8	20	12	8
Gravimetric (G) or volumetric (V)	G	V	V	V	V	V	G	V	V
CO_2	3·8	3·6	6·8	7·0	6·5	13·1	3·8	4·2	4·8
H_2O	9·5	9·5	17·6	13·1	12·3	7·7	14·9	16·0	15·9
CO	15·3	15·6	4·5	7·9	9·5	5·0	10·2	8·8	7·1
Hydrocarbon	0·8	1·3	*	*	*	0·6	*	*	*
H_2	9·5	9·4	3·9	5·4	5·8	0·64	10·9	9·3	7·7
N_2	61·1	60·6	67·2	66·2	65·6	73·1	60·3	62·0	64·4

From the above analyses it is evident that the gases in all cases were mainly carbon dioxide, water-vapour, carbon monoxide, and hydrogen, together with the nitrogen accompanying the air supply. In some cases a small quantity of "hydrocarbons" is set down. This is the most unsatisfactory feature in the analyses, for the uncertainty as to the nature and quantity of these hydrocarbons affects the whole analysis. It has been necessary in calculating the results to make some arbitrary assumption as to the nature of the hydrocarbons, and on this account, as well as from the fact that the substances employed were not in all cases pure, the analyses must only be considered as preliminary. It will be observed that variation in the diameter of the tubes has a considerable effect on the products of partial combustion. Diminution of diameter of the inner tube necessitates the employment of more air, and so increases the proportion of carbon dioxide and water formed. In no case was free oxygen found in the gases.

In the case of coal-gas, the mixture burning at the inner tube consisted of about 1 vol. of coal-gas to 4·8 vols. of air, and so contained about twice the normal amount of air for a Bunsen flame. In the case of benzene, the gas consisted of 1 vol. of benzene vapour to about 30 of air.

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* Quantity of hydrocarbons too small to estimate.

General Considerations on the Results obtained with Hydrocarbons.

From the foregoing results it is clear that when a hydrocarbon is burnt with air in sufficient quantity, the flame consists of two distinct hollow cones, the inner one tending to propagate itself downwards, the outer one tending in the opposite direction. This is indeed no new discovery, though we find that many chemists have been in the habit of regarding the Bunsen flame rather as a single mass of glowing gas with an inner and outer surface than as two cones of flame. Blochmann in his well-known paper (*Ann.*, **168**, 295) states explicitly that the flame has the two-coned structure. In an ordinary Bunsen flame these cones approximate to one another very closely, and only when the air supply is increased is their separate existence evident. The thickness of the walls of the cones is very slight, and this is particularly the case with the inner cone. It is bounded on the lower side by a ready-made explosive mixture, so that the chemical action is very intense and local. Outward from it proceed gases which have to make their own explosive mixture by diffusing with the outside air until the necessary oxygen is obtained. The large size, greater thickness, want of sharpness, and lower temperature of the outer flame are thus explained. The theory of the separation of these cones has already been given.

Perhaps the most remarkable fact apparent from our analyses is that the main chemical change occurring in the inner cone consists in the combustion of the hydrocarbons to form carbon monoxide and water with smaller quantities of carbon dioxide and hydrogen. But here again we find on referring to Blochmann's paper that he infers that this kind of change takes place in the ordinary Bunsen flame. The importance of his observation has no doubt been overlooked on account of the fact that he used coal-gas, which, in the unburned state, contains about half its volume of hydrogen. It is, at any rate, satisfactory to have proved the existence of such a change with definite hydrocarbons and in a perfectly direct manner.

At the time when we obtained these results we were not aware of what we have since found to be some well-established facts concerning the combustion of hydrocarbons with oxygen insufficient in amount for their complete oxidation to carbon dioxide and water. But a short time subsequently, after we had discussed the subject with Professor H. B. Dixon, it happened independently to him and to ourselves to discover that the incomplete oxidation of methane and ethylene had been studied at the beginning of the century. Dalton states that ethylene exploded with its own volume of oxygen gives carbonic oxide and hydrogen, and that marsh gas, under similar conditions, gives equal volumes of steam, carbonic oxide, and hydrogen.

$$C_2H_4 + O_2 = 2CO + 2H_2.$$
$$CH_4 + O_2 = CO + H_2O + H_2.$$

The incomplete combustion of these hydrocarbons was studied again in 1861 by Kersten (*J. pr. Chem.*, **84**, 310) who, in the main, substantiates Dalton's results although they were evidently unknown to him. Without reference either to Dalton or Kersten, the subject was again taken up in 1874 by E. von Meyer and similar results obtained, and at the same time, experiments of the same kind were made independently by Thomas.*

We do not think the explanation of the facts observed is difficult to find. That carbon on oxidation, even with excess of oxygen, burns first to carbon monoxide, is highly probable from the experiments of H. B. Baker (*Proc. Roy. Soc.*, 1889, **45**, 1), but that carbon should burn more readily than hydrogen, is not in accordance with a widely prevailing, though scarcely justifiable belief. Without desiring to raise any confusion between questions of affinity and of energy, we may be allowed to draw attention to the thermochemical aspect of the question.

The calculated heat of combustion of solid carbon to carbon monoxide is only 29,000 calories, but the thermal effect is here diminished by the amount of heat necessary for the gasification of solid charcoal, and accordingly we find that the addition of a second atom of oxygen (that is, the conversion of CO into CO_2) gives a much greater heat evolution, viz. 67,960 calories.

Attempts have been made† to calculate the heat of combustion of gaseous carbon to carbon dioxide, but objection has been taken to them‡ on the ground that they virtually assume the heat of combination of the first and second atoms of oxygen to be equal. But in any case it is agreed that the combination of the first atom of oxygen with a carbon atom produces at least as much heat as that of the second atom, viz., 67,960 calories, and this is more heat than is evolved in the combustion of hydrogen to gaseous water (57,900 calories). The last number is, however, the heat of combination of a *molecule* of hydrogen, and to it must be added the heat necessary for the separation of this molecule into atoms. No reliable estimate of this value has ever been made.

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* We are indebted to Professor Thorpe for drawing our attention to the work of Thomas, an account of which appears in *Iron*, 1875, and in an appendix to "Coal-mine Gases and Ventilation," by J. W. Thomas, Longmans and Co., 1878. On this point Professor Dixon writes to us: "In the spring of last year I determined the rate of the explosion-wave in a mixture of ethylene with its own volume of oxygen. I found *detonation* took place, and that the oxygen was entirely taken by the carbon setting hydrogen free, in accordance with Blochmann's equation and with E. von Meyer's results, which I doubted. After making these experiments, I happened to come across Dalton's work in the second part of his *New System*. I did not know that Kersten had done it; I have to thank you for calling my attention to his work."

† See especially Thomsen, *Thermochem-Untersuch.* Band IV.

‡ Armstrong, *Phil. Mag.* [5], 23, Feb. 1887.

We may suppose that in our experiments, when the hydrocarbon first burns in the inner cone, there is a distribution of the limited supply of oxygen between the carbon and hydrogen, such, that either carbon monoxide and water or carbon monoxide, water, and hydrogen are first formed. The two gases carbon monoxide and water, cannot exist at the temperature of the flame without a second interaction immediately taking place, whereby the former is oxidised by the latter with the production of the carbon dioxide and hydrogen. This, however, is a reversible change, and the decomposition is not complete. There thus remain four gases, carbon monoxide, hydrogen, carbon dioxide, and water, together with the nitrogen which accompanied the oxygen in the air-supply. The changes then would be as follows with methane:—

$$1.\ CH_4 + O_2 = CO + H_2O + H_2.$$
$$2.\ CO + H_2O \rightleftarrows CO_2 + H_2.$$

The conditions of equilibrium for this system of gases have been worked out by Dixon in his well-known memoir (*Phil. Trans.*, 1884, 618). It was, therefore, a matter of great interest to us to see to what extent we got a constant ratio of products, and how our ratios agreed with Dixon's constant. This, however, is one of the questions into which we do not feel at present prepared to enter. We will only remark that whilst Dixon gives the normal condition of equilibrium as follows $\frac{CO \times H_2O}{CO_2 \times H_2} = 4{\cdot}0$, we obtain from our most reliable analyses numbers not greatly differing from 4. More accurate analysis of the gases, the influence of differing diameters of the tubes, rates of efflux, and quantities of diluent gases are questions on which we are at present engaged, and demand careful study before we can put forward any conclusions on the question of equilibrium, which is perhaps the most interesting and important aspect of our work.

With regard to the relation of our results to those obtained by Blochmann in his experiments on the normal Bunsen flame, it has been already pointed out that there is substantial agreement on the main points. But, as in our experiments, the gases were burning with a much greater supply of air, the quantity of hydrocarbons passing the first area of combustion was in many cases practically *nil;* whereas in Blochmann's experiments as much as 8·7 per cent. of hydrocarbons was found in the interconal space at a height of 5 cm. above the burner. We hope eventually to repeat Blochmann's experiments, using a definite hydrocarbon instead of coal-gas.

It seems possible by means of our apparatus to gain precise information as to the mode in which ethylene and other hydrocarbons break up when burning with luminous flames. It has already been stated, that it is possible to separate the cones of the ethylene-air flame before they have become non-luminous, that is, while carbon is being separated in the flame, and it is obvious that by an accurate analysis of the gases under these circumstances it should be possible to determine whether the carbon is being separated by the simple decomposition of the ethylene into its elements, by its resolution into carbon and methane, by the preferential combustion of the hydrogen, or by some other decomposition. That the process is complex is probable from the fact that we have found acetylene in the interconal gases. We intend to try to repeat Landolt's experiments (Pogg, *Annalen*, **99**, 389) on the composition of gases from luminous flames, using ethylene instead of the complex coal-gas which he employed, but we are not very hopeful of gaining much information by this method.

Experiments with other Gases.

We have made a number of experiments with flames from substances other than hydrocarbons, and by supplying the mixed gas or vapour and air to the separating apparatus have "divided" the flames produced from decomposed ammonia (that is, $N_2 + 3H_2$), cyanogen, hydrogen sulphide, and carbon bisulphide.

With the mixture of hydrogen and nitrogen, obtained by passing ammonia through a hot tube, the phenomena is seen at its simplest, for here, in the first cone, the whole of the oxygen combines with hydrogen to form steam, which, with the nitrogen and excess of hydrogen, passes to the top of the outer tube, where this hydrogen burns with the outside air in a second flame.

With cyanogen* the phenomena are the most beautiful we have met with in the course of our experiments. The cyanogen, burning without added air, gives a flame with a rose-coloured central cone, and an outer cone shading from dark-blue to greenish-grey. As air is allowed to enter with the cyanogen, the margin of the inner cone assumes a deep, cherry-red tint, and it eventually descends to the inner tube. The outer cone, now of a blue-grey colour, remains on the outer tube. If more air is supplied, the upper cone becomes imperfect, being gathered in at the base and not in contact with the glass, whilst the inner cone grows greyer. Eventually the upper flame altogether disappears, the lower one becoming bluish-grey. A sample of gas from the interconal space, withdrawn when the two separated cones were perfect, was found, on analysis, to contain carbon monoxide and dioxide, almost exactly in the proportion of 2 vols. to 1. No cyanogen could be detected by smell or analysis.

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* As we had not a convenient apparatus for storing cyanogen, Professor Dixon very kindly allowed us to make the experiment in his laboratory at Manchester.

The combustion of cyanogen in a eudiometer with quantities of oxygen insufficient to convert the carbon wholly into carbon dioxide, was investigated by Bunsen (*Gasometrische Methode*, 2nd edition, p. 340). In two different experiments, he found the ratios of CO to CO_2 1 vol. to 2 and 2 vols. to 5.

In our experiments we have been able to use a much smaller proportion of oxygen than Bunsen found possible, and the results show, as we should expect, that the production of CO is relatively much greater.

The sulphuretted hydrogen flame, when produced in our apparatus, is easily divided into two cones. We have not yet made a quantitative analysis of the gases from the interconal space, but most of the sulphur appears to pass the first cone without undergoing combustion.

The flame from carbon bisulphide vapour can be divided in the same way as is adopted for liquid hydrocarbons, but we have not yet made a quantitative study of the process.

There is still much to be done with the apparatus described in this paper. We have already indicated some of the points that have to be worked out, and we conclude by briefly summarising them.

1. The influence of differences in the diameter of the tubes, and rates of efflux of the gases on the fractional combustion.

2. The exact analysis of the interconal gases in the case of hydrocarbons and of mixtures of CO and H_2, in order to ascertain if, and in what way, the coefficient $\frac{CO \times H_2O}{CO_2 \times H_2} = 4$ varies with the composition of the gases.

3. The analysis of the interconal gas from an ethylene flame whilst carbon is being liberated, so as to determine how the hydrocarbon breaks up.

4. The further study of the cyanogen flame.

5. To determine the partition of oxygen in the inner cone between carbon and hydrogen, hydrogen and sulphur, carbon and sulphur, and so obtain information of the relative affinities of these elements for oxygen.

XVI.—*Note on the Structure of Luminous Flames.*

By Arthur Smithells, B.Sc., The Yorkshire College, Leeds.

The following are extracts from Davy's book "On the Safety Lamp for Coal Miners, with some Researches on Flame" (1818), a reprint of his papers in the Philosophical Transactions and elsewhere.

(1.) "Flame must be considered as the combustion of an *explosive mixture* of inflammable gas or vapour and air, for it cannot be regarded as a mere combustion at the surface of contact of the inflammable matter, and the fact is proved by holding a taper or a piece of burning phosphorus within a large flame made by the combustion of alcohol, the flame of the candle or of the phosphorus will appear in the centre of the other flame, proving that there is oxygen even in its interior part.

(2.) "The form of flame is conical, because the greatest heat is in the centre of the explosive mixture. In looking steadfastly at flame, the part where combustible matter is volatilised is seen, and it appears dark, contrasted with the part in which it begins to burn, that is where it is so mixed with air as to become explosive. The heat diminishes towards the top of the flame, because in this part the quantity of oxygen is least.

(3.) "The luminosity of flames is due to 'the decomposition of part of the gas towards the interior of the flame where the air is in smallest quantity and the deposition of *solid charcoal*, which, first by its *ignition* and then by its *combustion*, increases in a high degree the intensity of the light.'

(4.) "At the bottom part of the flame where the gas burned blue in its immediate contact with the atmosphere, charcoal ceased to be deposited in visible quantities."

The above extracts contain the essence of all that Davy contributed to the subject of luminous flames so far as their structure is concerned.

The description of an ordinary luminous flame as consisting of the four parts now generally recognised, appears to have been first given by Berzelius. In the English edition (1822) of his work on "The Use of the Blowpipe" (p. 22), the following description occurs :—If we attentively consider the flame of a candle, we may remark several unequal divisions of it, of which four may be distinguished. We see at its base a small part of a dark-blue colour, which becomes thinner as its gets farther from the wick, and disappears entirely where the external surface of the flame ascends perpendicularly. In the middle of the flame is a dark place seen through its brilliant covering. This space encloses the gases which issue from the wick, which, not being yet in contact with the air, cannot undergo combustion. Round this space is the brilliant part of the flame, properly so called, and, lastly, beyond this we may perceive, by attentive inspection, the outer covering of all, slightly luminous, and whose greatest thickness corresponds with the summit of the brilliant flame. It is in this outer part that the combustion of gases is completed and the heat the most intense.

In a striking paper by D. Waldie (*Phil. Mag.*, 1838, **13**, 88), a description very like the above is to be found, but the author recognises a fifth area, namely, an area of unburned carbon. This seems to have been nothing more than the lurid and smoky tip of flame, which, in the days of tallow candles and straight wicks, was, perhaps, worthy of distinction.

In 1847, Volger published (*Pogg. Ann.*, 1847, 72—82) a highly speculative account of a candle flame, in which he distinguishes no less than six parts. It is, perhaps, unnecessary to discuss these views; they were never generally accepted, and rest upon assumptions which in many cases are obviously untenable.

I am not aware that anyone, since the last-named date, has deliberately put forward new views on the actual *structure* of flame, and it may be taken as a matter of general belief that there really are four regions in what is ordinarily called a luminous flame. For convenience we will name them according to their appearance, the dark region, the yellow region, the blue region, the faintly luminous region. These are shown in Fig 1.

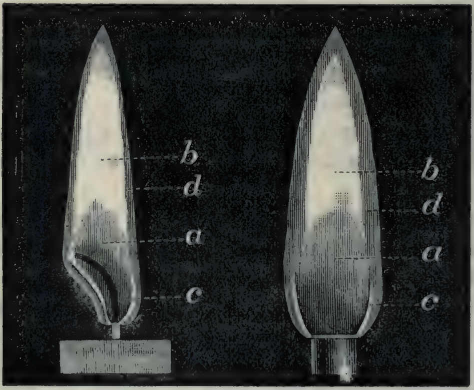

FIG. 1.—Sketches to scale of candle flame and small gas flame: *a*, dark region; *b*, yellow region; *c*, blue region; *d*, faintly-luminous region.

Whilst there has been general agreement as to the number of distinct parts in a luminous flame, there has been from time to time considerable difference of opinion as to the causes, whether chemical or otherwise, which give rise to or define them, and I will now give a brief summary of the views which have been held regarding each of the four parts of the flame.

The Dark Region or Zone of Unburned Gases.

All observers agree in regarding this as due to combustible gas in which no combustion is taking place. The fact that no combustion takes place in this part of a flame, or, in other words, that flames are hollow, was noticed by Francis Bacon.*

Hilgard, in 1854 (*Liebig's Annalen*, **92**, 129), showed that in a candle flame this region also contained nitrogen and products of combustion. He found in the lower parts 66 per cent. of nitrogen, 10 per cent. of carbon dioxide, 5 per cent. of carbon monoxide, 6 per cent. of water, and no free oxygen. The rest was combustible gas.

Landolt (*Pogg. Ann.*, **99**, 389) obtained similar results with a coal-gas flame, but found also a very small quantity of free oxygen in the lowest parts.

The Yellow Region.

Davy's explanation of the luminosity of ordinary flames has already been quoted (the exact wording should be carefully noticed), and this explanation, together with the general doctrine that the luminosity of flames is due to incandescent, solid particles, was not questioned until 1868, when Frankland showed (*Proc. Roy. Soc.*, **16**, 419) that flames containing only gaseous matter, for example, that of hydrogen in oxygen, could be made luminous by compression. Frankland also concluded that the luminosity of ordinary flames was due not to solid particles of carbon but to the incandescent vapour of dense hydrocarbons. This latter view was combated by several chemists, amongst whom Heumann is chiefly to be mentioned. In 1876, Heumann brought forward (*Liebig's Annalen*, **181**, 129 **182**, 1; or *Phil. Mag.*

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* "Take an arrow and hold it in flame for the space of ten pulses, and when it cometh forth you shall find those parts of the arrow which were on the outsides of the flame more burned blacked and turned almost into a coale; whereas that in the midst of the flame will be as if the fire had scarce touched it. This is an instance of great consequence for the discovery of the nature of flame, and sheweth manifestly that flame burneth more violently towards the sides than in the midst; and which is more, that heat or fire is not violent or furious but where it is checked and pent."—*Sylva Sylvarum or a Naturall History in Ten Centuries.* By Francis Bacon. 6th Ed. (1615), p. 9.

[5], **3** (1877), 1, 89, 366) a number of experiments and arguments in confirmation of Davy's view that the separation of solid carbon is the cause of the luminosity of ordinary flames. I am not aware that Heumann's conclusions on this point have ever been contested; they have, indeed, been confirmed by independent methods of experiment (see Soret, *Phil. Mag.*, 1875, 50; Burch, *Nature*, **31**, 272; Stokes, *ibid.*, **45**, 133).

The *cause* of the separation of carbon is another question. According to Davy it is due to the *decomposition* of the hydrocarbons within the flame, and though he adds the words "where the air is in smallest quantity," it is not explicitly stated that the decomposition is due to anything but the heat alone. No mention of any other cause is made by Berzelius, Waldie, Hilgard, Landolt, or any other author that I have been able to consult, so far as original memoirs are concerned. But prior to 1860 a view had become current that the separation of carbon in a luminous flame was due to the preferential burning of the hydrogen. There not being enough oxygen in the luminous region of a flame for the complete combustion of the hydrocarbons, it was inferred that the hydrogen, being the more inflammable element, burned first and so liberated the carbon. I have so far been unable to trace this doctrine to its source. It may have been an inference from Davy's words, but can scarcely be justified by them. He says nothing whatever as to what happens to the hydrogen when carbon is separated in a flame. Not only was this view generally maintained at the time alluded to, it survives at the present day and, as I can vouch from personal enquiries, it is still widely taught.

The doctrine in question was challenged in 1861 by Kersten (*J. pr. Chem.* **84**, 290), who pointed out that there was no *a priori* reason for believing hydrogen to be more combustible than carbon. He points out that whilst previous admixture with chlorine increases the luminosity of a methane flame by virtue of the superior affinity of chlorine for hydrogen, previous admixture with oxygen has the reverse effect. Again, a mixture of 1 volume of methane and 2 of carbon monoxide burns with a non-luminous flame, although it contains only enough oxygen for complete combustion of the hydrogen:—$CH_4 + 2CO = 2H_2O + 3C$; or again, the amount of oxygen necessary to produce a non-luminous coal-gas flame in a Bunsen burner is only one-third of the quantity necessary for complete combustion. Kersten remarks, as it appears to me, very justly, that the experiments of Hilgard and Landolt, in which gases were aspirated from luminous flames and then analysed, do not give any definite information as to the main chemical changes occurring in luminous flames. By the methods used by these investigators it is impossible to explore the luminous part of the flame, owing to the stopping up of the aspirating tube by carbon; nor can any precise information be gained as to the changes taking place in the external layer of the flame, owing to its movement and the infiltration of gases from within and without this layer. Kersten was accordingly led to make experiments on the explosion of hydrocarbons with quantities of oxygen insufficient for complete combustion, and (as mentioned in the preceding paper) he obtained results directly opposed to the view that the hydrogen burns preferentially to the carbon. He concluded, therefore, that the separation of carbon in a flame was due simply to the decomposition of the hydrocarbons by heat.

I have not met with any explicit contradiction of Kersten's views, but they seem to have been neglected to a remarkable extent by subsequent writers.

The *glow* of the carbon in the yellow region is due to the heat of its own combustion, and is increased probably by the concomitant combustion of hydrogen. The view occasionally met with, that the carbon is glowing only by the heat of the burning hydrogen, is manifestly erroneous. The carbon is in the solid state, and must either undergo the usual glowing combustion, or else escape from the flame unburned. As it does not do the latter to any appreciable extent, it must burn, and the cessation of its combustion as a solid marks the limit of the yellow or luminous region of the flame.

The Blue Region.

The blue region has been unanimously regarded as a part of the flame where the hydrocarbons are mixed with sufficient air to cause immediate combustion without the separation of carbon.

The Faintly Luminous Region or Mantle.

This part of the flame was not referred to by Davy as distinct from the blue region. Berzelius describes it, and states that "it is in this outer part that the combustion of the gases is completed and the heat the most intense." Waldie states that it consists of "the proper combustible mixture," and is the hottest part of the flame, and that to its heat is to be attributed the separation of the carbon within the flame.

No intelligible distinction appears to have been made between this region and the blue one until 1861, when Kersten published the paper already referred to, and even his description is not easy to grasp. He appears to have regarded the faintly luminous region as the place in which hydrogen and carbon monoxide coming from the yellow region undergo combustion, ignoring the fact that it surrounds not only the yellow region, but the blue one as well.

I have only met with one other attempt to explain this part of a luminous flame as distinct from the blue portion, and have not been able to trace it beyond the text-books. It ascribes this faintly luminous region to products of combustion (carbon dioxide and water) mixed with air and raised to feeble incandescence, that is, it is not a region of chemical action at all. If for no other reason, this explanation could scarcely be maintained in face of the observations made by Siemens (*Ann. Phys. Chem.*, **18**, 311), that such products of combustion have not perceptible luminosity at 1500°.

Having thus summarised the views hitherto held regarding the parts of a luminous flame, I will now submit the matter to a brief discussion from a different point of view.

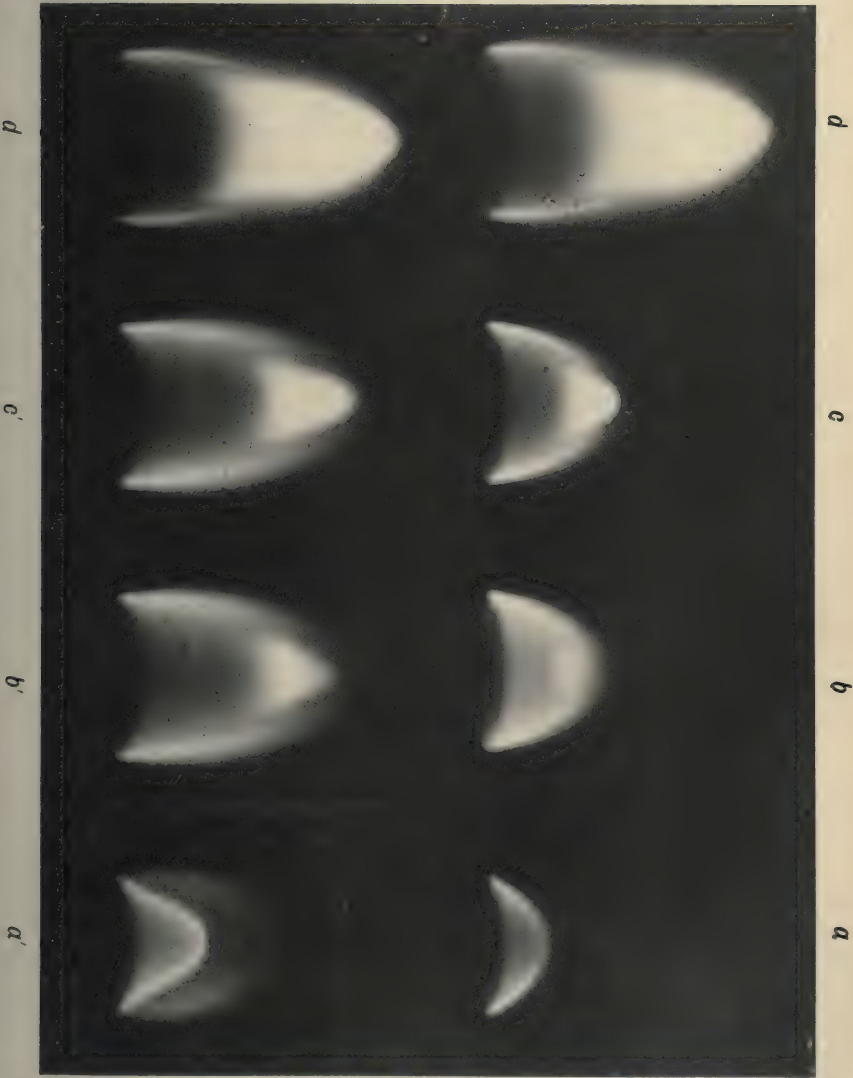
The best way to study flame structure seems to me to consist in tracing the development of the flame. By using a very small quantity of combustible, that is to say, in the case of gases, by almost turning off the tap, and, in the case of solids and liquids, by having a very close cropped wick, we obtain a tiny flame which is ordinarily called non-luminous. It has the appearance represented in Plate II, *a*, and consists of a hollow, bright-blue cone, surrounded by a lilac-coloured border. If more gas be turned on, or if the wick becomes longer, a luminous spot is developed in the flame, as shown in Plate II, *b*. This spot is at first a small fraction of the whole flame, but as the supply of combustible is increased it rapidly extends, as shown in Plate II, *c* and *d*, the original inner cone becomes a "vestige," and forms, in fact, the blue region. Still the original formation is evident, the luminous spot being indented at points corresponding to it.

The question now arises, is the non-luminous flame *a* a single or a double cone, and, in any case, what chemical changes are taking place in it?

I think an answer to this question may be obtained by carefully watching the change undergone by a luminous flame when air is gradually added to the gas prior to combustion. For this purpose a small flame from a Bunsen burner, with the air-holes at first closed, may be employed. If attention be fixed on the blue and on the faintly luminous regions of the flame, and the air-holes be now slowly opened, the flame loses luminosity, and the two regions grow more distinct, and ultimately become, without any perceptible break of continuity in the process, the inner and outer cones of the ordinary Bunsen flame.

These changes are shown in Plate II, taken from photographs; *a*, *b*, *c*, and *d* show the gradual development of a luminous flame as the gas is turned on. The blue region of the flame appears white, but it is easily distinguishable from the yellow region which also appears white. The lilac or faintly luminous region is barely visible

Journ. Chem. Soc. March, 1892. PLATE II.



in the pictures, as it has very low photographic power. c', b', a' represent the flame d with gradually increasing quantities of air admitted through the air valves, the gas supply being kept constant. The structure of c and c', b and b', a and a' obviously corresponds. In a' the outer cone has just impressed an image on the photographic plate.*

If the conclusion be admitted that the blue and the faintly luminous regions of an ordinary flame correspond to the inner and outer cones of a Bunsen flame, then, in accordance with the results detailed in the preceding paper, we must consider the blue region to mark *incomplete* combustion (CO, H_2, CO_2, and H_2O being the chief substances there originating), and the faintly luminous part to mark *completed* combustion (the CO and H_2 above named being burnt to CO_2 and H_2O).

In other words, I conclude that there is no essential difference in kind between an ordinary luminous flame and a so-called "non-luminous" flame. The latter may be regarded as a gas-air flame with the blue and the non-luminous regions at a maximum, and the yellow, luminous region at a minimum, whilst the luminous flame is to be regarded as a gas-air flame with the blue and the non-luminous parts at a minimum and the yellow luminous region at a maximum.

As it has been repeatedly shown that the dark, central part of a luminous flame is a region of no combustion, there only remains now one question for solution—how is the carbon separated in the yellow, luminous region? It would seem scarcely necessary after a perusal of Kersten's paper (*loc. cit.*) to argue this point at any length. The doctrine that the hydrogen of a hydrocarbon burns before the carbon when the supply of oxygen is limited is not borne out by any experiments of which I am aware, with the possible exception of those of Berthelot and Vieille (*Compt. rend.*, **98**, 705—711; this Journal, Abstr., 1884, 804). From the fact that the velocity of explosion of hydrocarbons rich in hydrogen approximates to that of hydrogen itself, they conclude that the hydrogen burns before the carbon. The experiments of Dalton, Kersten, E. von Meyer, and those recorded in the preceding paper, all point to exactly the opposite conclusion, namely, that the carbon burns preferentially to the hydrogen. If this conclusion is accepted, we can only explain the separation of carbon in a luminous flame as due to a *decomposition by heat*, whereby a given hydrocarbon is split up into carbon and hydrogen or carbon and some more richly hydrogenised hydrocarbons. Hydrocarbons are well known to undergo such decompositions when passed through hot tubes.

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* I am largely indebted to the skill and patience of Mr. Herbert Ingle for these photographs, as well as for those used in the preceding paper.

A very simple experiment, which seems sufficient to prove the truth of this view, is made by introducing a circular loop of thin wire into any small gas flame in which the luminous part is only slightly developed. The immediate result is that the luminous part disappears and the flame presents the simple structure of a non-luminous flame, at the same time becoming slightly larger. This change is represented in Fig. 2.

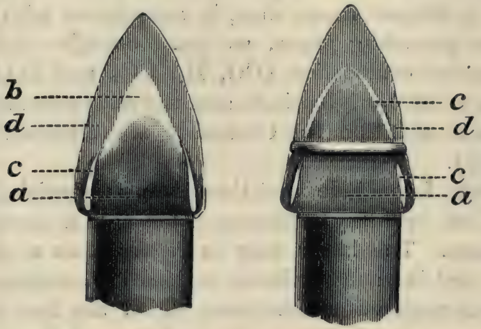

FIG. 2.—*a*, the dark region; *b*, the yellow region; *c*, the blue region; *d*, the faintly luminous region.

Now if the flame is luminous because, the hydrocarbons in the middle being short of oxygen, the hydrogen burns first, the intrusion of the wire will block out and still further limit the supply of oxygen, and so either increase the area of luminosity or cause the escape of unburned carbon.

If, on the other hand, the luminosity is due to the heat of the external perfectly burned layers decomposing the hydrocarbons, then the intrusion of the wire by tapping the heat should diminish the luminosity, and the hydrocarbons which previously gave light should pass on until they obtain enough oxygen to burn as those hydrocarbons on the exterior of the flame. The flame, therefore, would become larger and non-luminous. This is exactly what happens in the experiment.

The above experiment only holds good if the wire conducts heat away at a certain rate. If the flame be relatively large, the introduction of the wire may produce an opposite effect, for, whilst checking the separation of carbon (to an appreciable extent), it will also cool down the carbon which is separated, and so cause some of it to escape unburned as smoke.

A problem remaining to be studied concerns the exact course of the decomposition of the hydrocarbon in the flame, and the only method available seems to be the one alluded to in the preceding paper.

By taking an ethylene-air flame, and separating the cones before the luminosity has entirely disappeared, an examination of the interconal gases under these conditions will disclose what is being produced along with the separated carbon, and in this way I hope to trace the course of the decomposition. As the matter rests at present, the development of a luminous hydrocarbon flame may be described as follows:—

The hydrocarbon issues from the burner or wick, let us suppose, as a cylindrical column. This column is not sharply marked off from the air, but is so penetrated by the latter that we must suppose a gradual transition from the pure hydrocarbon in the centre of the column to the pure air on the outside. Let us take a thin, transverse slice of the flame, near the lower part of the wick or close to the burner. At what lateral distance from the centre will combustion begin? Clearly where enough oxygen has penetrated the column to give such partial combustion as takes place in the inner cone of a Bunsen burner. This, then, defines *the blue region.* Outside this, the combustion of the carbon monoxide, hydrogen, and any hydrocarbons which pass from the blue region takes place, and constitutes the *faintly luminous region.* These two layers form a sheath of active combustion, surrounding and intensely heating the hydrocarbons in the central parts of the column. These heated hydrocarbons rise, and are heated to a higher temperature as they ascend. They are accordingly decomposed with the separation of carbon in the higher parts of the flame, giving us the *yellow region,* but there remains a central core in which neither is there any oxygen for combustion nor a sufficiently high temperature for decomposition. This constitutes the *dark region* of unburned gases. A flame is, however, not cylindrical, but has a conical or (in the case of a candle) an inverted peg-top shape. Again, the blue region only surrounds the lower part of the flame, whilst the faintly luminous part surrounds the whole. The above explanation is, therefore, not quite complete. Let us suppose that the changes have gone on in the small section of the flame exactly as described, and consider how the processes will differ in parts above this section. The central core of unburned gases will pass upwards, and we may treat it as a new cylindrical column which will undergo changes just as the original one, leaving, however, a smaller core of unburned gases, or, in other words, each succeeding section of the flame will be of smaller diameter. This gives us the conical structure of the flame. Again, the higher we go in the flame, the greater proportionally is the amount of separated carbon, for we have not only the heat of laterally outlying combustion to effect decomposition, but also that of the *lower* parts of the flame. The lower part of a luminous flame is accordingly cooler, and contains less separated carbon than the upper. Now, where the hydrocarbons are cool until admixed with sufficient air for combustion (that is, in the lower parts of the flame), we have every facility for the occurrence of the chemical changes to which the existence of the blue region has been ascribed, and the blue region is here most evident; whereas in the upper parts of the flame, where the quantity of hydrocarbon decomposed (with separation of carbon) by heat is relatively much greater, there is not enough left to form outside the yellow part the mixture to which the blue region of flame is due. The blue region, therefore, rapidly thins off as we ascend the flame. But whether the first combustion taking place within the flame is that of the undecomposed hydrocarbon with limited oxygen, or of the decomposed hydrocarbon with limited oxygen, we may be sure that the products will contain carbon monoxide, and probably hydrogen, and we shall therefore have *all round the flame* a faintly luminous region of completed combustion. In this way, then, we may reasonably account for the existence, position, and relative sizes of the four regions of an ordinary luminous flame.

XVII.—*The Composition of Cooked Vegetables.*

By Miss Katharine J. Williams, Associate of University College, Bristol.

The investigations described in the following pages were undertaken at the suggestion of Dr. Ramsay, in order to obtain information as to the composition of foods as served at table; for, as previous work on this subject deals mainly with analysis of raw vegetables, little is known as to the changes produced during the processes of cooking. The vegetables used were bought when in full season, except the scarlet runners and salsify, which were kindly supplied by friends. The potatoes, vegetable marrows, and tomatoes were cooked and dried in September, 1886, the broad beans, green peas, and spinach in July, 1887.

General Preparation of the Samples used.

The chief consideration was to obtain a sample of each vegetable just as it would be served on table; the scarlet runners were cut into long slips; the pods of the broad beans and green peas were removed before cooking; such vegetables as cabbage, vegetable marrow, and parsnips were prepared in the usual manner for boiling, but no soda was added to the water in which they were cooked. The water in which they were boiled was undistilled, as supplied by the Bristol Water Company, and shows about 26 degrees of hardness, chiefly due to calcium carbonate.

To give minute details as to the uncooked vegetables, the tomatoes and cucumbers used were peeled before drying; the skin of the mushrooms was carefully removed; the radishes were washed, all green parts removed, and the roots scraped; and the celery was washed and the green tops cut off; the lettuce was carefully washed.

Determination of Water.

Every sample of the vegetables, whether cooked or raw, was cut into small pieces or mashed up, and the surface water removed before the process of drying was commenced. When cool, a small portion of each vegetable was weighed, and placed, with the evaporating dish it was on, inside a steam-bath, the temperature of which was kept at about 100°; after 12 or more hours had elapsed, it was allowed to cool in a desiccator, weighed again, reduced to powder in a coffee-mill, the residue weighed again, then dried in an air-bath at a temperature not exceeding 130° until the weight remained constant, and from these results the percentage of water was calculated.

The table below shows the percentage of water found, and, for the sake of comparison, results obtained by others with vegetables in the uncooked condition are given; those for cauliflower and radish are taken from *Die Menslichen Nährung und Genussmittel*, Dr. J. König; those for green peas from *Wurtz's Dictionary;* and the rest from Professor Church's work on *Foods.*

TABLE I.

	Cooked.	Raw.		Cooked.	Raw.
Potato (boiled in skin).	73·80	75·0	Carrots............	93·45	89·0
Potato (boiled without skin)............	76·27	—	Cauliflower..........	96·46	90·89
Tomato..............	94·07	89·8	Vegetable marrow.....	99·17	94·8
Scarlet runners........	91·12	91·8	Spanish onions.......	98·69	—
Cabbage..............	97·45	89·0	Parsnips............	97·28	82·0
Cucumbers............	97·48	96·2	Jerusalem artichokes..	91·69	80·0
Mushrooms...........	97·97	90·0	Haricot beans........	73·62	14·0
Beet-root............	94·81	82·2	Sea-kale............	97·95	93·3
Radish..............	94·93	93·31	Turnips............	97·25	92·8
Lettuce..............	97·21	96·0	Spinach............	98·07	90·0
Celery..............	97·05	93·3	Green peas..........	86·91	9·7
Salsify..............	87·29	—	Broad beans.........	86·59	—

As a general rule, the amount of water in the cooked vegetables exceeds that in the raw condition, except in the case of potatoes, which are but little altered by boiling. The starch here probably forms a protecting skin, which prevents gain or loss of water. The analyses given of uncooked beans and peas obviously refer to dry parched samples, and not to the fresh vegetables.

ULTIMATE ANALYSIS.

Carbon and Hydrogen.

The carbon and hydrogen were estimated by the usual method of combustion with copper oxide, using a current of dried oxygen; the resulting water was collected in a chloride of calcium tube, and the carbon dioxide in potash bulbs. A few ultimate analyses of sugar were made to secure the proper working of the apparatus. At least three determinations were made with each vegetable in the dried and finely-powdered condition. A few details will give some idea as to the concordance of individual results with each other.

	Carrots.		Scarlet runners.		Celery.	
	Hydrogen.	Carbon.	Hydrogen.	Carbon.	Hydrogen.	Carbon.
	5·70	40·86	6·32	43·86	5·71	41·01
	5·98	41·24	6·51	43·54	5·75	41·48
	6·10	41·25	6·35	43·55	5·94	41·32
Mean..	5·93	41·11	6·39	43·65	5·80	41·27

TABLE II.—*Percentage of Hydrogen and Carbon.*

	Hydrogen.	Carbon.		Hydrogen.	Carbon.
Potato (boiled in skin)	5·75	40·07	Carrots	5·93	41·11
Potato (boiled without skin)	5·39	35·50	Vegetable marrow	5·67	44·52
Tomato	5·65	47·74	Cauliflower	6·40	40·97
Scarlet runners	6·39	43·65	Spanish onions	5·87	47·61
Cabbage	6·26	43·72	Parsnips	6·03	45·38
Cucumber	5·30	48·69	Jerusalem artichokes	6·25	42·17
Beet-root	6·17	44·01	Haricot beans	6·10	44·64
Mushrooms	5·98	42·42	Sea-kale	5·50	44·61
Radish	4·58	36·39	Turnips	6·77	41·71
Lettuce	5·71	40·62	Spinach	5·18	31·10
Celery	5·80	41·27	Green peas	6·97	39·31
Salsify	6·14	42·52	Broad beans	6·70	41·29

It is to be remarked that the carbon and hydrogen do not vary within very wide limits; the exceptionally high percentage of carbon in cucumber may be noticed, as also the low percentages in potatoes boiled without the skin, and in spinach.

Total Nitrogen.

Dumas' method was used in the estimation of nitrogen. The substance was burnt in a tube containing copper oxide and copper gauze, the tube being first cleared of air by a current of carbon dioxide evolved from potassium hydrogen carbonate. The volume of nitrogen was duly corrected for temperature and pressure. In the first few, and in doubtful cases, two estimations were made. One example of the results will show the concordance obtained.

	I.	II.	Mean.
Haricot beans	6·33	6·51	6·42 per cent.

TABLE III.—*Percentage of Nitrogen.*

Potato (in skin) ...	2·04	Radish	4·84	Jerusalem artichokes	4·20
Potato (without skin)	2·40	Lettuce	3·87	Haricot beans	6·42
Tomato	3·45	Celery	2·67	Sea-kale	6·60
Scarlet runners	3·38	Salsify	2·23	Turnips	1·99
Cabbage	4·24	Carrots...........	2·27	Spinach	6·67
Cucumber	3·80	Vegetable marrow	3·32	Green peas	5·26
Beet-root..........	1·82	Cauliflower	4·45	Broad beans	5·28
Mushrooms..........	8·93	Spanish onions...	1·66		
		Parsnips	1·96		

The nitrogen is seen to be very variable, its percentage ranging from 1·66 in onions to 8·93 in mushrooms.

Determination of Ash.

The first determinations of the ash were made by burning a weighed portion of the substance in a platinum boat placed inside a glass tube through which a current of oxygen was passing; it was, however, found that by careful manipulation satisfactory results could be obtained by weighing the residue left after the estimation of the carbon and hydrogen. At least two determinations were made with each vegetable. Examples of the results are given below.

	Cucumber, Method I. Per cent.
I	10·60
II	10·81
Mean.	10·70

	Celery, Method II. Per cent.
I	18·88
II	18·86
III	19·08
Mean.	18·94

The table given below shows the percentage of ash found in each case, and also the work of other analysts collected from the same sources as the results given in Table I (p. 227). The figures given refer in each case to percentages in the dry substance of the vegetables analysed.

TABLE IV.—*Percentage of Ash.*

	Cooked.	Raw.		Cooked.	Raw.
Celery	18·94	11·9	Beet-root	7·54	5·05
Radish	17·82	11·1	Cabbage	7·20	10·9
Lettuce	16·99	25·0	Vegetable marrow	6·28	9·61
Tomato	12·88	7·84	Onions	5·59	5·6
Turnip	11·75	11·11	Potato (in skin)	4·85	4·0
Spinach	11·31	20·0	Scarlet runners	4·38	7·8
Cucumber	10·70	10·5	Parsnips	4·38	5·05
Mushrooms	10·42	7·0	Broad beans	3·53	—
Sea-kale	10·10	8·95	Potato (without skin)	2·95	—
Carrots	7·55	9·0	Salsify	2·92	—
Jerusalem artichokes	7·45	5·5	Haricot beans	2·66	3·37
Cauliflower	7·55	9·1	Green peas	2·57	2·76

Estimation of Sulphur.

To ascertain if the sulphur present was contained in the ash alone, experiments were made with cabbage and onions as typical vegetables. A weighed portion of the ash left, after combustion in oxygen, was fused with a mixture of sodium carbonate and potassium nitrate in a platinum crucible, and the remaining mass was dissolved in water, acidified with nitric acid, and the sulphur estimated as barium sulphate. A weighed portion of the dried vegetable was next treated in a similar way; and the results obtained by these two methods were:—

	Cabbage.	Onions.
Method I	3·85	0·56 per cent.
Method II	3·71	0·55 „

Experiments were also made which gave for radish 0·58, and for cauliflower 0·68 per cent.; but, as these results were so low, and the sulphur was mainly found in the ash, no further investigations were made in this direction.

Proximate Analysis.

The details given above with regard to the percentages found for ash and water also belong to this division of the subject.

Woody Fibre.

The process of determining woody fibre has been much improved since this work was done, but it would be impossible to revise it, using the same samples. The results may, at all events, be regarded as comparative.

The method used in this portion of the work was that depending on treatment with sulphuric acid, as described by Dr. Percy F. Frankland in his *Agricultural Chemical Analysis*, founded upon Dr. F. Krocker's *Leitfaden der Agricultural chemische Analyse.* From 4 to 8 grams of the powdered vegetable were placed in a flask with 50 c.c. of a solution of sulphuric acid (50 grams of the strong acid diluted to 1000 c.c.), 150 c.c. of water added, the whole boiled for half an hour, and then cooled; the liquid was siphoned off, a small funnel, covered with fine muslin, being placed on the shorter arm of the siphon. The residue was boiled twice with 200 c.c. of distilled water, and then with 50 c.c. of potassium hydrate (50 grams per litre) diluted with 150 c.c. of water; after this, it was again twice boiled with water, the boiling in each case lasting for half an hour, the supernatant liquid being each time siphoned off befere the fresh addition of water. The residue was next thrown on a weighed filter, and washed in succession with hot water, alcohol, and ether, and then dried at 110° in an air-bath. A soda-lime combustion was made in order to estimate any albuminoïd matter left in the residue, and the ammonia evolved collected in nitrogen bulbs containing hydrochloric acid of a known strength, the excess of the acid being neutralised by sodium hydrate, and the weight of the nitrogen found being multiplied by 6·25 to obtain the percentage required. A portion of the residue was also estimated for ash, the total percentage, *minus* the albuminous matter and ash, being taken as woody fibre.

TABLE V.—*Woody Fibre.*

	Per cent.		Per cent.		Per cent.
Sea-kale	23·06	Broad beans	13·72	Salsify	7·76
Turnip	23·00	Tomato	12·79	Mushrooms	6·60
Celery	20·75	Green peas	12·63	Jerusalem artichokes	4·70
Cauliflower......	18·88	Beet-root	11·57	Haricot beans...	3·86
Cabbage	18·43	Carrots	11·53	Potato (in skin).	1·86
Radish	18·53	Spinach.........	11·52	Potato (without skin)	0·70
Vegetable marrow	16·45	Parsnips	11·25		
Scarlet runners ..	15·04	Lettuce	10·57		
Cucumber.......	13·26	Onions	8·75		

One estimation for each vegetable was found sufficient after the first two, except in a very few cases. As an example, celery may be quoted; the total residue was 23·15 per cent.; of this 1·16 per cent. was albuminoïd matter, and 1·24 per cent. ash, thus leaving 20·75 per cent. as woody fibre.

Albuminoïds.

The percentage of albuminoïds was determined as before by soda-lime combustion, two determinations being made for each vegetable. While working on this part of the subject, attention was directed to the fact already known, that in the case of many vegetable products the amount of nitrogen evolved by the soda-lime process was, in almost all instances, lower than that found by Dumas' method; as the four examples below will show.

	Soda-lime method.	Dumas' method.		Soda-lime method.	Dumas' method.
Celery........	1·72	2·67	Beet-root	1·40	1·82
Tomato........	2·90	3·45	Cabbage	2·92	4·24

To be quite certain that no mistake had been made with the copper oxide series of combustions, fresh determinations were made with the same samples of vegetables. The second set of results agreed very closely with the first; for example, green peas gave 5·26 and 5·06; vegetable marrow, 3·32 and 3·24 per cent.; but in case of different samples of the same vegetables, very different results were obtained with those collected in 1888 from those collected in 1887.

	Dumas' method, 1887.	Dumas' method, 1888.	Soda-lime method, 1888.
Sea-kale........	6·60	4·34	3·22
Parsnips	1·96	2·40	1·42
Potato..........	2·04	1·70	0·99

This merely confirms the fact already long known, that the percentage of nitrogen varies with (*a*) the maturity of the plant, (*b*) the variety of the plant, (*c*) the soil and cultivation, (*d*) the season.

It is well known that certain organic substances do not yield the whole of their nitrogen as ammonia on combustion with soda lime, but, as Professor Church states in his work on *Foods*, some of the nitrogen is contained in the form of nitrates and of other non-albuminoïd compounds.

TABLE VI.—*Albuminoïds.*

	Per cent.		Per cent.		Per cent.
Mushrooms	52·13	Lettuce	18·93	Salsify	9·56
Cauliflower	26·31	Tomato	17·78	Parsnips	8·62
Cabbage	24·27	Haricot beans	17·52	Beet-root	8·59
Radish	23·07	Broad beans	15·85	Carrots	8·15
Jerusalem artichokes	21·84	Spinach	15·17	Potato (boiled without skin)	6·70
Cucumber	21·51	Spanish onions	11·96	Potato (boiled in skin)	6·17
Green peas	21·29	Vegetable marrow	11·85		
Scarlet runners	20·63	Turnips	11·77		
Sea-kale	20·16	Celery	10·40		

Nitrates.

The difference in the percentage of nitrogen evolved by Dumas' and the soda-lime methods pointed to the necessity of determining the amount of nitrates present. A good deal of work in this direction has been done by various English and German chemists, and investigations made as to the change of nitrates into albuminoïds during various stages of plant growth. In the *Comptes rendus*, **98** (1884), Berthelot gives full particulars as to work on plants, and in the *Comptes rendus*, **99** (1884), a joint paper of his and G. André contains a good deal of information as to the presence of nitrates.

Following the directions given in these papers, a few grams of the dried vegetable were in each case digested with dilute alcohol (60 : 40 water) in a flask connected with a reflux condenser, to dissolve the nitrates and coagulate the albuminoïds; after filtration, the filtrate, if acid, was neutralised with potassium carbonate and evaporated to dryness over a water-bath. Two solutions were prepared in every case, but only such vegetables as showed deficiency in nitrogen by the soda-lime combustion were examined. The nitrates were estimated by means of Warington's modification of Schloesing's method (Sutton's *Volumetric Analysis*, edition 4, p. 210) by means of ferrous chloride. An oil-bath was used instead of the bath of calcium chloride solution advised, as it was found to be more under control. A few experiments were made with potassium nitrate to secure the proper working order of the apparatus. The nitric oxide evolved was collected over mercury in a graduated tube, and the usual corrections made for temperature and pressure. A few examples will show the concordance of the results obtained.

	Broad beans.	Sea-kale.	Jerusalem artichokes.
	2·41	2·84	2·60 per cent.
	2·46	2·83	2·66 ,,
Mean..	2·43	2·83	2·63 ,,

TABLE VII.—*Nitrogen calculated into Potassium Nitrate.*

	Per cent.		Per cent.		Per cent.
Vegetable marrow	12·04	Carrots	4·35	Parsnips	1·97
Spinach	12·06	Salsify	3·76	Cucumber	1·93
Lettuce	5 96	Tomato	3·58	Haricot beans....	1·89
Celery	5·28	Sea-kale	2·84	Potato (without skin)	1·68
Turnips	5·14	Jerusalem artichokes	2·63	Radish	1·21
Beet-root	5·51	Broad beans	2·43	Potato (boiled in skin)	0·32
Green peas	4·99				

Cellulose.

This estimation was made by means of the potassium chlorate method originally suggested by F. Schulze (*Chem. Centr.*, 1857, 321). From 2 to 4 grams of the dried and powdered vegetables were in each case digested with 12 parts of nitric acid (sp. gr. 1·10) and 0·8 part of potassium chlorate in a closed flask; to prevent the temperature rising above 15°, the flasks were placed in a vessel containing running water. This process lasted for about a fortnight. Distilled water was then added, and the liquid siphoned off; the residue was washed first with hot and then with cold water, which in each case was siphoned off; next the residue was washed into a beaker with dilute ammonia (1 part strong ammonia to 50 of water), and heated for about 45 minutes at 60°; the residue was thrown on a weighed filter, and washed with the same dilute ammonia, until the filtrate came through colourless; it was then washed successively with cold and with hot water, alcohol, and ether; it was finally dried and weighed. Any nitrogenous matter and ash present were estimated by the usual methods. The results are as follows:—

TABLE VIII.—*Cellulose.*

	Per cent.		Per cent.		Per cent.
Haricot beans	39·71	Radish	27·73	Carrots	16·76
Spinach	38·78	Lettuce	23·90	Celery	16·05
Sea-kale	33·99	Cucumber	22·97	Parsnips	15·71
Scarlet runners	33·32	Turnips	22·07	Beet-root	14·58
Cabbage	33·28	Onions	19·87	Mushrooms	14·02
Broad beans	32·93	Potato (boiled in skin)	17·21	Tomato	13·97
Cauliflower	32·92	Potato (boiled without skin)	16·83	Salsify	9·69
Green peas	29·86			Jerusalem artichokes	6·82
Vegetable marrow	29·08				

Fat.

The fat and colouring matters were extracted from the powdered vegetables by ether. From 2 to 5 grams were placed in a wide, glass tube, the narrower and lower end of which passed through the cork of a small flask of about 100 c.c. capacity, containing the ether, whilst the upper end of the tube was connected with a reflux condenser. The flask was heated by a water-bath, the ethereal vapour dissolving the oil of the vegetable as it passed over it; fresh ether was used from time to time until a drop on evaporation left no residue; when all the soluble matter had been extracted, the ether was distilled off and the residue was weighed. At least two estimations were made in every case, and fairly satisfactory results as to concordance were obtained.

	Turnip.	Tomato.	Lettuce.	
	2·37	3·71	5·84	per cent.
	2·22	3·89	5·94	„
Mean...	2·29	3·80	5·89	„

TABLE IX.—*Fat.*

	Per cent.		Per cent.		Per cent.
Spinach	9·43	Vegetable marrow	2·88	Cucumber	1·07
Lettuce	5·89	Carrots	2·63	Jerusalem artichokes	0·98
Mushrooms	5·50	Celery	2·31	Onions	0·91
Cabbage	4·83	Turnips	2·30	Salsify	0·72
Parsnips	4·33	Broad beans	2·12	Green peas	0·67
Tomato	4·32	Haricot beans	1·97	Potato (boiled in skin)	0·29
Scarlet runner	3·80	Radish	1·27	Potato (boiled without skin)	0·14
Sea-kale	3·47	Beet-root	1·15		
Cauliflower	3·32				

Glucose.

The final investigation of the carbohydrates convertible into glucose proved to be almost the most troublesome part of the whole work. At first the usual method given in text books (Church's *Laboratory Guide*, p. 233) was employed, but, on titrating with Fehling's solution, a blue or white precipitate came down. After several abortive attempts had been made, a modification of the method was tried, and proved successful. The conversion was made by hydrochloric acid, as usual, but instead of neutralising with sodium hydrate, the solution was treated with basic lead acetate, and, after filtration, a current of sulphur dioxide was passed through the liquid to precipitate any excess of lead present. The solution was then filtered, concentrated at 100°, and a little washed alumina added until no more was dissolved; the liquid was again filtered, and, if necessary, evaporated down to a smaller volume. As all the solutions were dark coloured, it was necessary to boil them before adding a few drops of milk of lime and powdered animal charcoal. After decolorisation, the solution was filtered and its volume measured; two solutions were prepared from each vegetable. The Fehling's solution used was prepared in the usual manner, and standardised according to the directions given by Roscoe and Schlorlemmer in their *Treatise on Chemistry*, vol. III, Part 2, p. 519. Difficulties in the titration were found in several cases, as the precipitate had constantly to be filtered off, otherwise it dissolved, whilst a white precipitate came down, and the solution turned to a vivid green. Among the solutions which behaved thus were those of spinach, cucumber, and celery. A good example of the results obtained is that of sea-kale.

I. 2·88568 grams taken. Volume of solution, 115·9 c.c.
II. 3·55348 grams taken. Volume of solution, 135·9 c.c.
10 c.c. Fehling = 0·040285 gram of invert sugar.

	I.			II.		
	Fehling.		Glucose.	Fehling.		Glucose.
	10 c.c.	=	10·14 c.c.	10 c.c.	=	8·98 c.c.
	10 ,,	=	9·41 ,,	10 ,,	=	9·27 ,,
	10 ,,	=	9·46 ,,	10 ,,	=	9·28 ,,
Mean..	10 ,,	=	9·67 ,,	10 ,,	=	9·17 ,,

On calculation, percentage of glucose found:—

I.	II.	Mean.
16·73	16·79	16·76

TABLE X.—*Glucose or Carbohydrates converted into Glucose.*

	Per cent.		Per cent.		Per cent.
Potato (boiled in skin)	79·46	Jerusalem artichokes	37·19	Cucumber	17·72
Potato (boiled without skin)	79·25	Green peas	36·06	Sea-kale	16·76
Salsify	56·97	Haricot beans	34·48	Radish	14·54
Parsnips	53·94	Broad beans	32·04	Cabbage	14·36
Onions	53·10	Vegetable marrow	25·17	Cauliflower	13·08
Carrots	51·90	Turnip	23·65	Celery	13·06
Beet-root	44·19	Scarlet runners	22·70	Mushrooms	12·78
				Lettuce	12·17
				Tomato	10·85
				Spinach	4·66

On adding up the total proximate results, it was seen that in the case of certain vegetables they were low; some carbohydrates present in various vegetables are not convertible into compounds capable of reducing Fehling's solution, but possibly here certain compounds, such as the pectins, had not been converted into glucose by the above method. Fresh solutions were therefore prepared, as suggested by Sachsse (*Chem. Centr.*, 8, 639 and 732), by digesting the vegetables with rather stronger hydrochloric acid, 10 c.c. (sp. gr. 1·125), and 10 c.c. water, in a flask connected with a reflux condenser; the whole was boiled briskly over a water-bath for three hours, and the solution was then filtered and treated with basic lead acetate, &c., as described previously. The table shows the results obtained by this method.

TABLE XI.—*Glucose prepared by the more Rapid Method.*

	Per cent.		Per cent.
Salsify	63·48	Cucumber	27·99
Jerusalem artichokes	55·91	Tomato	25·05
Beet-root	54·59	Lettuce	20·66
Celery	29·38	Spinach	12·18
Vegetable marrow	29·04		

As stated in the beginning of this paper, the work here described was undertaken with the idea of arriving at a clearer knowledge of the composition of vegetables as eaten; therefore it is difficult to compare the results obtained with those of other investigators; for even in the raw condition great differences in composition occur. A few vegetables such as celery, lettuce, radishes, and mushrooms are included, although these were not previously cooked; they are chiefly interesting for the sake of comparison with the work of others in the same direction. With the exception of mushrooms, two samples at least of every vegetable have been used, and in the case of potatoes seven or eight; as this was the vegetable easiest to procure, nearly all the first determinations were made with it. This fact is mentioned, as it may partly account for the high total results obtained with some of the series. It will be noticed that in the case of almost all vegetables the percentage of water is higher in the cooked than in the uncooked condition, especially in the leguminous class.

For the sake of comparison, Table XII has been drawn up from *Die Menschlichen Nährung und Genussmittel*, by Dr. König (Edition 1882–83), also Table XIII from *Food*, by Professor Church (Edition 1889). (The vegetable marrows and cucumbers were peeled before the analyses were made.) Table XIV contains a list of the same vegetables, the constituents of which were determined by the author; the results have been calculated on the materials in their natural moist condition.

TABLE XII.—*Proximate Analysis taken from König's "Die Menschlichen Nährung und Genussmittel."*

	Analysis.	Water.	Albuminoïds.	Fat.	Sugar.	Other carbo-hydrates free from nitrogen.	Phosphorus.	Sulphur.	Woody fibre.	Ash.
Potato maximum	90	82·86	3·66	0·31	—	21·24	—	—	1·37	1·45
Potato minimum	—	68·20	0·57	0·03	—	18·75	—	—	0·28	0·53
Potato mean....	—	75·45	1·95	0·15	—	20·69	—	—	0·75	0·98
Cabbage	8	85·89	2·87	0·21	0·38	7·80	0·12	0·06	1·68	1·17
Celery (without green)	—	89·57	0·88	0·34	0·62	5·94	trace	—	1·24	1·46
Celery...........	1	84·09	1·48	0·39	0·77	11·03	0·74	0·21	1·40	0·84
Cucumber........	3	95·60	1·02	0·09	0·95	1·33	...	—	—	0·39
Tomato..........	—	92·87	—	0·33	2·53	1·54	—	—	0·84	0·64
Lettuce..........	5	94·33	1·41	0·31	—	2·19	0·09	0·01	0·73	1·03
Radish	—	94·31	1·15	0·09	1·14	1·97	—	—	0·65	0·67
Mushrooms	1	98·34	3·39	0·07	—	2·39	—	—	0·54	0·76

The last two vegetables were analysed by W. Dahlen; one analysis of cucumber was made by R. Pott, who found 97·19 per cent. water; ash, 0·24; albuminoïds, 0·60 per cent.

TABLE XIII.—*From Professor Church's "Food."*

	Water.	Albuminoïds, &c.	Starch.	Fat.	Sugar.	Cellulose.	Mineral matter.	Extractives.	Dextrin pectose gum.
Haricot beans	14·0	23·0	52·3	2·3	—	5·5	2·9	—	—
Potatoes	75·0	1·2	18·0	0·3	—	1·0	1·0	*1·5	2·0
Turnips.....	92·8	0·5	—	0·1	—	1·3	0·8	†1·0	3·0
Carrots	89·0	0·5	—	0·2	4·5	2·3	1·0	—	2·5
Parsnips	82·0	1·2	3·5	1·5	5·0	2·1	1·0	—	3·7
Beet-root ...	82·2	0·4	10·0	0·1	—	3·0	0·9	†1·0	2·4
Jerusalem artichokes...	80·0	2·0	—	0·5	4·2	2·0	1·1	Inulin 1·1	9·1
Cabbage	89·0	1·5	‡5·8	0·5	—	2·0	1·2	—	—
Sea-kale.....	93·3	1·4	§2·8	—	—	0·9	0·6	—	—
Vegetable marrow ...	94·8	0·6	0·6	0·2	2·0	1·3	0·5	—	—
Tomatoes ...	89·8	1·4	—	—	6·0	1·8	0·8	Malic acid 0·7	—
Celery......	93·3	1·4	§1·6	—	2·0	0·9	0·8	—	—
Lettuce.....	96·0	0·7	‡1·6	0·2	—	0·5	0·1	—	—
Cucumber...	96·2	0·2	—	—	2·0	0·5	0·4	—	0·7

* As solanine and organic acids. † Including amides.

‡ Starch, gum, and sugar. § Mucilage, starch, &c.

TABLE XIV.—*Proximate Analysis.*

	Water.	Ash.	Albuminoïds.	Woody fibre.	Fat.	Cellulose.	Glucose.	Potassium nitrate.
Cabbage	97·45	0·13	0·61	0·47	0·12	0·84	0·36	—
Lettuce	97·21	0·47	0·52	0·29	0·16	0·66	0·57	0·16
Tomato	94·07	0·76	1·05	0·75	0·25	0·82	0·11	0·21
Celery	97·05	0·55	0·30	0·61	0·06	0·47	0·86	0·15
Radish............	94·93	0·90	1·17	0·94	0·06	1·40	0·73	0·06
Mushroom	97·97	0·03	1·57	0·18	0·16	0·42	0·38	—
Haricot beans.........	73·68	0·70	4·61	1·01	0·52	10·45	9·07	0·46
Turnips............	97·25	0·32	0·32	0·63	0·06	0·60	0·65	0·14
Carrots	93·45	0·14	0·53	0·75	0·17	1·09	3·39	0·28
Parsnips	97·28	0·12	0·23	0·30	0·29	0·42	1·46	0·05
Beet-root............	94·81	0·38	0·44	0·60	0·06	0·75	2·83	0·26
Sea-kale............	97·95	0·20	0·41	0·47	0·07	0·69	0·34	0·05
Vegetable marrow.....	99·17	0·05	0·09	0·13	0·04	0·24	0·24	0·09
Cucumber............	97·48	0·27	0·54	0·33	0·02	0·57	0·70	0·04
Potato (boiled in skin) .	73·80	1·27	1·62	0·49	0·03	4·50	20·81	0·08
Jerusalem artichokes...	91·69	0·61	1·81	0·39	0·08	0·56	4·64	0·21

Heats of Combustion.

In this section of the work, the method adopted was that described by W. Thomson in a paper, "On a New Apparatus for readily determining the Calorific Value of Fuel or other Organic Substances by Direct Combustion," published in the *Journal of the Society of Chemical Industry*, Vol. V, No. 11. The water value of the apparatus used was carefully calculated according to the directions given in the article, as the table below will show.

TABLE XV.—*Water Value of the Apparatus Used.*

Material used.	Weight in grams.	Specific heat of the material.	Equivalent in grams of water.
Glass of beaker	323·8957	0·1977	47·70
Glass bell	27·0083	0·1977	5·33
Brass tube	12·6900	0·0939	1·19
Brass stand and springs	50·3675	0·0939	4·72
Copper gauze	66·6901	0·0951	6·34
Thermometer glass	4·1500	0·1977	0·82
Mercury	8·2920	0·0333	0·27
Clay support	7·7946	0·1977	1·54
Platinum crucible	6·1659	0·0324	0·20
India-rubber	1·2109	0·2000	0·24
Water employed	—	—	2500·00
Total equivalent of water in calorimeter	—	—	2568·05

In order to compare the results obtained with those of other workers in this department, and to secure accurate results, a series of experiments was first made with cane sugar and starch.

TABLE XVI.

	Highest.	Lowest.	Mean of some experiments.
Cane sugar	4063·0	3954·0	4034·3
Starch	4322·7	4215·9	4285·0

The results given below show what has been done by others. F. Stohmann's determinations are to be found in the *Zeitschrift für physikalische Chemie*, II Band, 1 Heft, 1888; while those of Berthelot and Vieille and Rechenberg are calculated from numbers given in the *Comptes rendus*, **102**, 1284.

	Berthelot and Vieille.	Rechenberg.	Stohmann.
Starch	4228·0	4481·0	4121·0
Cane sugar	3961·7	4145·0	3840·0

After the preliminary experiments were finished, and the apparatus was found to be in good working order, investigations were begun with the prepared vegetables, at least three determinations being made in every case. A few examples will show their agreement one with another.

Haricot beans.	Spinach.	Cauliflower.	Sea-kale.
4435·6	4262·8	4476·0	4634·1
4446·3	4300·2	4479·7	4664·7
4386·6	4262·6	4500·4	4650·1
4446·5	4297·5	—	—
4454·3	—	—	—
4445·3	—	—	—
Mean.. 4435·76	4280·6	4485·3	4646·3

TABLE XVII.—*Heats of Combustion.*

Names of vegetables.	Heats of combustion.	Names of vegetables.	Heats of combustion.
Sea-kale	4646·3	Potato (boiled in skin)	4072·6
Cauliflower	4485·3	Parsnips	4044·2
Haricot beans	4435·76	Cucumber	4025·7
Tomato	4431·6	Beet-root	3992·9
Broad beans	4425·6	Turnip	3891·3
Green peas	4317·7	Mushrooms	3868·7
Spinach	4280·6	Potato (boiled without skin)	3819·0
Vegetable marrow	4266·4	Jerusalem artichokes	3818·0
Cabbage	4100·3	Carrots	3660·6
Onions	4105·9	Lettuce	3642·1
Scarlet runner	4104·9	Celery	3623·7
Salsify	4084·3	Radish	3246·0

The heats of combustion can be calculated from the ultimate analyses of the vegetables, on the assumption that the carbon exists as graphite, and the hydrogen is free except that portion already in combination with oxygen. It is to be noticed that in all cases a higher result is obtained than that actually found. The differences may be viewed as the heats of formation of the vegetables from their ultimate constituents, and it is evident that heat would be evolved were they to be thus synthesised, if such a synthesis were conceivable.

XVIII.—*The Dissociation of Liquid Nitrogen Peroxide.*

By W. Ostwald.

Mr. Cundall has recently (Trans., 1891, **59**, p. 1076) published an account of an interesting series of observations on the dissociation which nitrogen peroxide undergoes when dissolved in chloroform. As, according to Van't Hoff, dissolved substances obey the same laws as gases, and the laws of dissociation of binary compounds, such as nitrogen peroxide, are well known for the gaseous state, it is to be expected that the same laws should hold good for the dissolved peroxide.

The law of diesociation in the gaseous state is expressed by the equation :—

$$\frac{x^2}{1 - x} = \mathrm{K}v,$$

where x is the amount of dissociated, and $1 - x$ the amount of undissociated peroxide, v the volume of unit mass, and K a coefficient depending chiefly on the temperature, but constant at constant temperature.

As Van't Hoff's generalisation is applicable only to dilute solutions, it is necessary to refer to Table III of Mr. Cundall's paper (*loc. cit.*, p. 1086). In column II are given the percentage strengths of solutions, whose reciprocals are equal to $100/v$ of our equation. The last column, multiplied by 0·000468 (compare p. 1089), gives the quantity x. If we denote by c the concentrations (col. II) of the solutions, and by r the relative amount of NO_2 (col. IV), we obtain by putting $c = 100/v$ and $x = 0{\cdot}000468r$.

$$\frac{0{\cdot}000468r^2 . c}{1 - 0{\cdot}000468r} = 100\mathrm{K}.$$

Since K is constant at constant temperatures, the first member of the equation must also be constant. By making use of the figures of Table III, we obtain :—

c.	*v.*	*x.*	K
9·93	3·8	0·00178	0·000000312
6·0	4·4	206	254
4·8	4·5	211	213
3·6	5·7	267	257
2·5	6·5	304	231
2·0	7·0	328	215
1·6	8·06	377	227
1·4	8·7	407	228
0·8	11·2	524	220

It is obvious that nitrogen peroxide does indeed dissociate in accordance with the same law, whether it be in dilute solution or in the gaseous state, for the figures of the last column must be regarded as constant. The differences from the mean value 0·000000231 are quite irregularly distributed, and therefore could only be due to experimental errors, whose influence is nearly doubled in the calculation of the constant K. The first value alone seems to show too great a deviation, but the concentration of 10 per cent., corresponding to a pressure of more than 20 atmospheres, certainly exceeds the limits within which the simple laws of the gaseous state are valid.

It is a matter of interest to ask if the ratio of dissociation of the peroxide is the same in the gaseous and the dissolved state at equal concentrations, and, if not, in which of the two it is the greater. From the very accurate measurements made by E. and L. Natanson (*Ann. Phys. Chem.*, 1886, **27**, 606), we learn that, at 0° and at a pressure of 250 mm., the amount of dissociated peroxide amounts to as much as 10 per cent. For this state, the absolute density of the peroxide is 0·0014, that is, the gas corresponds to a 0·14 per cent. solution of peroxide in a vacuum. Now, according to Cundall, a 1·44 per cent. solution at 0° contains $5{\cdot}85 \times 0{\cdot}0468 = 0{\cdot}274$ per cent. of dissociated peroxide; according to the above-mentioned law, a 0·14 per cent. solution would therefore contain $\sqrt{10} \times 0{\cdot}274 = 0{\cdot}96$, or about 1 per cent. of dissociated peroxide. For the gaseous state, the dissociation is, therefore, far more advanced than in a chloroform solution; to reach the effect of a vacuum, the solution must be diluted to more than the hundredfold bulk of the gas.

It is to be expected that other solvents will show other relations, and it would be interesting to compare one solvent with another. It would not be surprising if the power of promoting dissociation should turn out to be closely connected with the property of promoting chemical change, as measured by N. Menschutkin (*Zeit. physikal. Chem.*, 1887, **1**, 627; 1890, **6**, 41). But it must, of course, be left to Mr. Cundall to extend the investigations, so happily begun by him, over a wider field.

In the paper under consideration, there is also some material for the comparison of the influence of temperature in both cases, the dissolved and the gaseous condition of the peroxide. On this occasion I shall not enter on the discussion of this question; the first problem is whether the temperature exerts the same influence with various solvents, or not, and before we know something on this point, a fruitful discussion can hardly be undertaken.

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XIX.—*Corydaline.* Part I.

By JAMES J. DOBBIE, M.A., D.Sc., and ALEXANDER LAUDER, University College of North Wales, Bangor.

THE rare alkaloïd corydaline was discovered by Wackenroder in the year 1826 in the tubers of *Corydalis tuberosa* (*Kastner's Archiv*, **8**, 423), and in the course of the next 40 years was investigated by numerous chemists, who failed, however, to arrive at a satisfactory conclusion with regard to its formula. In 1866, Wicke published in the *Annalen*, **137**, 274, a more complete and careful account of the alkaloïd than had hitherto appeared, accompanied by numerous analyses of the base and its compounds; from these he deduced the formula $C_{18}H_{19}NO_4$, which has since been accepted as representing correctly the composition of the alkaloïd.

Before beginning an investigation of the decomposition products of corydaline, we subjected several samples to analysis, and came to the conclusion that Wicke's formula is incorrect. The corydaline with which we experimented was obtained from Schuchardt, of Görlitz, in different lots, prepared at different times from the dried roots of *C. tuberosa*, gathered partly in the Tyrol and partly in Thuringia. The various samples were examined and analysed separately with the view of establishing definitely the identity of the alkaloïd obtained from different sources. After numerous experiments, we found that a mixture of absolute alcohol and ether, as recommended by Wicke, is the best solvent for corydaline. Such a solution rapidly assumes a yellow colour on exposure either to light or heat, and when employed for the crystallisation of the alkaloïd, must be kept in a cool, dark chamber. This susceptibility of corydaline to the action of light and heat probably accounts for the difficulty which earlier experimenters experienced in purifying this alkaloïd. The yellow resin with which they supposed it to be contaminated in the later stages of purification was no doubt an alteration product due to the action of light or heat, from which there is no evidence to show that they were careful to protect their solutions. In the paper already quoted, Wicke says: "The further purification of the crystals offered special difficulties, since the yellow colour could not be got rid of either by repeated crystallisation, or by treatment with freshly ignited animal charcoal." The former method of treatment would, in the presence of light, give rise to the production of the yellow matter from which it was intended to free the alkaloïd, and the treatment with animal charcoal, if carried out in the usual way, would produce the same result.

When crystallised with the precautions described, corydaline forms perfectly colourless, flat, prismatic crystals, which sometimes measure an eighth of an inch in length, and are, like their solution, quickly coloured yellow by the action of light or heat. Pure corydaline, when heated, changes colour about 125°, softens about 133°, and melts finally at 134·5°. We were unable to detect any difference in the melting point of the various samples experimented with when they were examined under similar conditions. The melting point given by Wicke is 130°. Corydaline dissolves easily in ether, chloroform, carbon bisulphide, and benzene, but less readily in alcohol. It also dissolves in oil of turpentine, yielding a yellow solution. Corydaline is practically insoluble in cold water, and only very slightly soluble in boiling water. From a pure alcoholic solution, water precipitates it in the crystalline form. It is soluble in dilute hydrochloric and sulphuric acids. When heated with dilute nitric acid, nitrous fumes are evolved, and a small quantity of the alkaloïd dissolves, forming a blood-red solution. Corydaline which has been coloured yellow by the action of light or heat is more easily soluble in alcohol or ether than the unaltered alkaloïd. A small quantity of corydaline was heated on the water-bath for two hours at 80—90°. It became yellow, and on treatment with a mixture of ether and alcohol, the yellow portion dissolved easily to a yellow solution, leaving unaltered corydaline behind, which, when treated with the same solvent, dissolved yielding a colourless solution. We were able to make use of this in purifying the alkaloïd, as we found it easy to remove a large part of the yellow substance by moistening with alcohol and ether and pressing between filter paper. Wicke has probably been misled by this difference between the solubility of altered and unaltered corydaline, when he states that alcohol dissolves pure corydaline with difficulty, although it dissolves corydaline which is mixed with resinous matter with great ease. We have further found that solutions of the purest corydaline rapidly become yellow on heating, although Wicke states that they remain colourless. The solution of corydaline in alcohol or ether has an alkaline reaction and a bitter taste.

The following are the results of the analysis of the pure alkaloïd (dried over strong sulphuric acid) carried out in the usual way:—

I. 0·2389 gram corydaline gave $\begin{cases} 0·17005 \text{ gram } H_2O = 7·90 \text{ p. c. H. (A.)} \\ 0·6245 \text{ gram } CO_2 = 71·29 \text{ p. c. C. (A.)} \end{cases}$

II. 0·23325 „ „ $\begin{cases} 0·1656 \text{ gram } H_2O = 7·88 \text{ p. c. H. (A.)} \\ 0·6119 \text{ gram } CO_2 = 71·54 \text{ p. c. C. (A.)} \end{cases}$

III. 0·2504 „ „ $\begin{cases} 0·1740 \text{ gram } H_2O = 7·72 \text{ p. c. H. (B.)} \\ 0·6569 \text{ gram } CO_2 = 71·54 \text{ p. c. C. (B.)} \end{cases}$

IV.	0·2413 gram corydaline gave	0·1660	gram H_2O	= 7·65 p. c. H.	(B.)
V.	0·20805 ,, ,,	0·5433	gram CO_2	= 71·21 p. c. C.	(C.)
VI.	0·2374 ,, ,,	0·1639 0·62075	gram H_2O gram CO_2	= 7·67 p. c. H. = 71·31 p. c. C.	(D.) (D.)
VII.	0·4396 ,, ,,	0·1156	gram Pt	= 3·84 p. c. N.	(A.)
VIII.	0·4549 ,, ,,	0·1214	,,	= 3·85 p. c. N.	(B.)
IX.	0·4558 ,, ,,	0·1230	,,	= 3·89 p. c. N.	(B.)
X.	0·4188 ,, ,,	0·1206	,,	= 3·68 p. c. N.	(B.)
XI.	0·3802 ,, ,,	0·1012	,,	= 3·83 p. c. N.	(C.)
XII.	0·4559 ,, ,,	0·1212	,,	= 3·83 p. c. N.	(D.)

The mean of these numbers* is :—

Carbon	71·37 per cent.
Hydrogen	7·76 ,,
Nitrogen	3·82 ,,

from which we deduce the formula $C_{22}H_{28}NO_4$.

	Found.	Theory for $C_{22}H_{28}NO_4$.	Theory for Wicke's formula, $C_{18}H_{19}NO_4$.
Carbon	71·37 p. c.	71·36 p. c.	69·00 p. c.
Hydrogen ..	7·76 ,,	7·57 ,,	6·07 ,,
Nitrogen....	3·82 ,,	3·78 ,,	4·47 ,,
Oxygen	17·05 ,,	17·29 ,,	20·46 ,,
	100·00	100·00	100·00

Wicke's formula, $C_{18}H_{19}NO_4$, is only supported by two determinations of carbon and hydrogen and one of nitrogen, which agree, however, with his theoretical numbers.

Corydaline forms a large number of salts and derivatives, most of which can be prepared without difficulty. The hydrochloride and sulphate are difficult to crystallise on account of the tendency of their solutions to become gummy. For this reason, and because the hydrochloride contains water of crystallisation, we selected the hydriodide for analysis.

Corydaline Hydriodide.—This salt is very easily prepared by adding a solution of potassium iodide to a solution of the hydrochloride in water. The hydriodide separates out in pale-yellow flocks which redissolve readily in hot water, and crystallise out, on cooling, in clusters of lemon-yellow, short, prismatic crystals. The specimen used for analysis was purified by repeated recrystallisation from water, and dried at 100°. The results obtained are as follows :—

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* The letters A, B, C, D, attached to the above analyses refer to the samples analysed.

I.	0·3017 gram salt gave	0·1590	gram H_2O	= 5·85 p. c. H.
		0·5896	gram CO_2	= 53·29 p. c. C.
II.	0·3098 ,, ,,	0·1625	gram H_2O	= 5·82 p. c. H.
		0·60525	gram CO_2	= 53·28 p. c. C.
III.	0·4832 ,, ,,	0·0924	gram Pt	= 2·75 p. c. N.
IV.	0·3907 ,, ,,	0·0750	,, Pt	= 2·76 p. c. N.
V.	0·4799 ,, ,,	0·2279	gram AgI	= 25·65 p. c. I.
VI.	0·4718 ,, ,,	0·2232	,, AgI	= 25·34 p. c. I.

	Found. (Mean of above analyses.)	Theory for $C_{22}H_{28}NO_4{\cdot}HI$.
Carbon....	53·28 per cent.	53·03 per cent.
Hydrogen .	5·83 ,,	5·80 ,,
Nitrogen ..	2·75 ,,	2·81 ,,
Iodine	25·49 ,,	25·47 ,,

The iodine, or other halogen, was determined in this and in other compounds containing them by heating the substance with pure lime and precipitation with nitrate of silver. The hydrobromide and hydrocyanide are prepared in the same way as the hydriodide, which they resemble in appearance and properties. Wicke analysed the hydrochloride and sulphate, but did not determine the carbon, hydrogen, and nitrogen in these salts. His determinations of chlorine agree well with his formula.*

Corydaline Platinochloride.—This salt is prepared in the pure state, suitable for exact analysis, by adding a solution of chloroplatinic acid, prepared by the action of chlorine and strong hydrochloric acid on

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* Wicke describes two chlorides, one containing 5 mols. H_2O, one without water of crystallisation, and one sulphate without water of crystallisation. The results of his analyses of these salts are as follows :—

Hydrochloride (without water of crystallisation).

	Found.	Theory for $C_{18}H_{19}NO_4{\cdot}HCl$.
Corydaline	89·00 per cent.	89·53 per cent.
Hydrochloric acid	10·40 ,,	10·47 ,,
	99·40 ,,	100·00 ,,

Sulphate.

	Found.	Theory for $C_{18}H_{19}NO_4,H_2SO_4$.
Corydaline	76·00 per cent.	76·15 per cent.
Sulphuric acid ...	23·23 ,,	23·85 ,,
	99·23 ,,	100·00 ,,

The corydaline in both cases was determined by precipitation with ammonia.

pure spongy platinum, to a solution of pure corydaline in dilute hydrochloric acid. It has a pale buff-yellow colour, which deepens to orange-red on continued heating in the water-bath at 100°. It is soluble in hot water, from which it separates, on cooling, in brown crystals. The sample used for analysis, after precipitation, was washed with cold water until the washings were free from acid. The following are the results of the analysis of the salt dried at 100°:—

I. 0·2855 gram salt gave $\begin{cases} 0·1344 \text{ gram } H_2O = 5·23 \text{ p. c. H.} \\ 0·4853 \text{ gram } CO_2 = 46·35 \text{ p. c. C.} \end{cases}$
II. 0·4332 ,, ,, 0·0795 gram Pt = 2·64 p. c. N.
III. 0·4112 ,, ,, 0·0739 ,, Pt = 2·58 p. c. N.
IV. 0·2843 ,, ,, 0·2084 gram AgCl = 18·12 p. c. Cl.
V. 0·2368 ,, ,, 0·1769 ,, AgCl = 18·45 p. c. Cl.
VI. 0·2433 ,, ,, 0·0414 gram Pt = 17·01 p. c. Pt.
VII. 0·2919 ,, ,, 0·0498 ,, Pt = 17·06 p. c. Pt.
VIII. 0·2755 ,, ,, 0·0465 ,, Pt = 16·84 p. c. Pt.
IX. 0·3035 ,, ,, 0·0511 ,, Pt = 16·83 p. c. Pt.

	Found. (Mean of above analyses.)	Theory for $(C_{22}H_{28}NO_4)_2,H_2PtCl_6$.
Carbon....	46·35 per cent.	45·92 per cent.
Hydrogen..	5·23 ,,	5·04 ,,
Nitrogen ..	2·61 ,,	2·44 ,,
Platinum ..	16·93 ,,	16·94 ,,
Chlorine ..	18·28 ,,	18·52 ,,

Corydaline Methiodide.—This compound is obtained by dissolving corydaline in methyl iodide. The excess of methyl iodide employed must be removed by spontaneous evaporation, since distillation under the ordinary atmospheric pressure invariably decomposes the compound. Corydaline methiodide dissolves in absolute alcohol, from which it crystallises in radiating tufts of pure white, needle-shaped crystals. Analysis of this derivative, dried at 100°, yielded the following results:—

I. 0·3259 gram salt gave 0·1744 gram H_2O = 5·94 p. c. H.
II. 0·2777 ,, ,, $\begin{cases} 0·1486 \text{ gram } H_2O = 5·95 \text{ p. c. H.} \\ 0·5441 \text{ gram } CO_2 = 53·43 \text{ p. c. C.} \end{cases}$
III. 0·4427 ,, ,, 0·0827 gram Pt = 2·91 p. c. N.
IV. 0·4368 ,, ,, 0·0881 ,, Pt = 2·89 p. c. N.
V. 0·4121 ,, ,, 0·1892 gram AgI = 24·79 p. c. I.
VI. 0·4960 ,, ,, 0·2261 ,, AgI = 24·63 p. c. I.

	Found. (Mean of above analyses.)	Theory for $C_{22}H_{28}NO_4 \cdot CH_3I$.
Carbon	53·43 per cent.	53·92 per cent.
Hydrogen .	5·95 ,,	6·05 ,,
Nitrogen ..	2·90 ,,	2·73 ,,
Iodine	24·71 ,,	24·79 ,,

The compound with allyl iodide was prepared in the same way as the methyl derivative. Like the methyl compound, it dissolves easily in absolute alcohol, from which it crystallises in beautiful, prismatic crystals of a brown colour.

When heated with hydrogen iodide, one formula weight of corydaline gives 4 mols. of methyl iodide, and yields the hydriodide of a base which apparently bears the same relation to corydaline that papaveroline bears to papaverine. On oxidation with potassium permanganate, corydaline yields a mixture of acids, which we are now engaged in investigating. We propose in a future paper to give the results of these experiments, together with fuller information as to the alkaloïd.

XX.—*Some Silver Compounds of Thiourea.*

By J. Emerson Reynolds, M.D., D.Sc., F.R.S.

At the conclusion of a paper on some derivatives of thiourea, published in 1888 (Trans., **53**, 857), I pointed out out that a definite crystalline compound of silver bromide with thiourea,

$$(CSN_2H_4)_2AgBr,$$

was obtained by the interaction of silver nitrate with $(CSN_2H_5)_4NBr$ in equal molecular proportions.

It was further stated that analogous compounds with other silver salts had been obtained by the same method, as well as by direct union with thiourea, and that the examination of these compounds in some detail had cleared up certain obscure facts which were simply recorded in my earlier papers on thiourea.

I did not intend to publish details of the examination of these silver compounds of thiourea until a similar examination could be made of the more interesting gold and platinum derivatives. But the recent appearance of a paper by Kurnakow (*Ber.*, **24**, 3956) on the silver compounds of thiourea renders further delay undesirable, as the Russian chemist refers only to the paper in which I described thiourea 22 years ago, and not to any later ones on the subject. Hence in the following pages will be found the details of the work on silver compounds referred to in 1888.

Kurnakow's communication being almost exclusively concerned with the products of the action of silver nitrate on thiourea, I shall first give the notes of my results in that direction.

Compounds of Silver Nitrate with Thiourea.

The white precipitates which can be obtained on mixing aqueous solutions of silver nitrate and thiourea vary in composition with the proportions of the reagents used, and gradually decompose when washed with water. If, however, alcohol be substituted for water, a perfectly definite crystalline compound can be prepared, containing three mols. of thiourea to one of silver nitrate.

17 grams of silver nitrate were dissolved in alcohol, and added to a hot alcoholic solution of 30·4 grams of thiourea (1—4 mols.). The solution soon deposited a large quantity of beautiful silky crystals, which when collected, washed with cold alcohol, and recrystallised from hot, strong alcohol, afforded a pure product, which melted sharply at 141°. The fused product began to decompose at about 150°, sulphide of silver separating.

Analysis of the pure crystals gave the following data:—

I. 0·4934 gram gave 0·178 of AgCl.
II. 0·3758 " 0·683 of $BaSO_4$.
III. 0·3633 " 0 646 of $BaSO_4$.
IV. 0·3384 " 67·2 c.c. of N at 7° and 760·5 mm.

The results agree closely with the formula $(CSN_2H_4)_2AgNO_3$.

		Experiment.			
	Theory.	I.	II.	III.	IV.
Ag	27·13	27·15	—	—	—
S........	24·24	—	24·98	24·44	—
N........	24·52	—	—	—	24·2

If the above pure compound be boiled with strong alcohol for some time or be recrystallised from 50 per cent. alcohol, decomposition occurs, and a substance is obtained which is richer in silver, and approximates to the formula $(CSN_2H_4)_2AgNO_3$, but I have not obtained a pure compound of that composition.

On the other hand, when aqueous solutions of equimolecular proportions of silver nitrate and thiourea were mixed, a precipitate was obtained, which, when slightly washed, pressed, and dried, gave

43·16 per cent. of Ag, as against 43·9 per cent. of Ag required for the compound $CSN_2H_4,AgNO_3$. And this product, after free washing, was found to contain 46·3 per cent. of silver, indicating decomposition by the continued action of water. I, therefore, long since arrived at the conclusion that the silver precipitate mentioned in my paper of 1869 was a product of decomposition of the too carefully washed lower compound of silver nitrate and thiourea just referred to.

Kurnakow's more recent work (*loc. cit.*) has led him to substantially the same result respecting the silver precipitate I first described, and he has isolated and more fully analysed the compound $CSN_2H_4AgNO_3$, whose existence was indicated by my silver determination cited above. Moreover, by dissolving the 1 : 1-compound in aqueous solution of thiourea he produced the 1 : 3-substance which I formed more simply of direct union in alcoholic solution, and examined more fully than he has done.

The general result of both lines of work is therefore the complete identification of the compounds

$$(CSN_2H_4)_3AgNO_3,$$
$$CSN_2H_4AgNO_3,$$

whilst some evidence of the existence of the intermediate substance $(CSN_2H_4)_2AgNO_3$ has been obtained.

Silver Bromide and Thiourea.

It has been shown in a former paper, as already mentioned, that the cautious addition of silver nitrate in alcoholic solution to an equimolecular proportion of $(CSN_2H_5)_4NBr$, affords a liquid from which the compound $(CSN_2H_4)_2AgBr$ separates out in crystalline form.

A considerable quantity was also obtained in the following manner:—17 grams of silver nitrate were precipitated by potassium bromide; the resulting AgBr was thoroughly washed with water and lastly with rectified spirit. A hot solution of 30·4 grams of thiourea (4 mols.) in 300 c.c. of alcohol was gradually added to the moist silver bromide. The addition of 75 c.c. (= 1 mol.) of thiourea sufficed to completely change the pale yellow of the bromide to white, and solution only commenced when this point was passed, and was not complete until the whole of the thiourea was added, and the mixture was gently warmed. On standing over night, a crop of fine crystals separated, consisting of beautiful, prismatic needles. These were collected, washed with cold alcohol, in which they are almost insoluble, pressed, and dried for analysis. The pure crystals melt at 120—121° to a clear liquid, but on heating to 180—183° gas is evolved, and at 190° blackening occurs.

I. 0·4013 gram gave 0·1279 of Ag.
II. 0·6845 „ 0·3785 of AgBr.
III. 0·6325 „ 0·8775 of $BaSO_4$.
IV. 0·452 „ 63 c.c. of N at 9° and 762·5 mm.

These results agree with the formula $(CSN_2H_4)_2AgBr$.

	Theory.	Experiment.
Ag	31·76	31·87
Br	23·52	23·53
S............	18·82	19·07
N	16·47	16·72

This compound was partially decomposed by water, although it can be recrystallised from an aqueous solution of thiourea. By the action of much water, a white substance separated resembling the material formed when 1 mol. of thiourea was added to finely-divided silver bromide in the first instance. An estimation of silver in some of the latter, formed by digesting silver bromide with rather more than 1 mol. of thiourea, gave 42·45 per cent. of silver. The formula $CSN_2H_4,AgBr$ requires 40·93; so that the whitening effect of thiourea on silver bromide, in the first instance, is probably due to the nearly complete formation of a 1 : 1-compound, which latter then dissolves in the urea solution with the formation of the 1 : 2 crystalline substance ultimately separated from the liquid.

There is, therefore, evidence that silver bromide forms the two compounds with thiourea:—

$$(CSN_2H_4)_2AgBr, \qquad CSN_2H_4AgBr.$$

Silver Chloride and Thiourea.

14·3 grams of freshly precipitated and washed silver chloride were added to a hot alcoholic solution of 30·4 grams (4 mols.) of thiourea. Solution was nearly complete, and the filtered liquid, when cold, deposited a fine crop of colourless, needle-like crystals. These were washed thoroughly with cold alcohol, pressed, and dried for analysis.

The crystals melt at 170—171°, affording a clear liquid, but decomposition commences at 180°, much Ag_2S separating.

The analytical data obtained were:—

I. 0·251 gram gave 0·092 of Ag.
II. 0·3965 „ 0 1875 of AgCl.
III. 0·263 „ 0·4157 of $BaSO_4$.

These numbers agree with the formula $(CSN_2H_4)_2AgCl$.

	Theory.	Experiment.
Ag	36·54	36·65
Cl	12·01	11·69
S............	21·65	21·73

This is identical with the substance obtained by Volhard (*J. pr. Chem.* [2], **9**, 14).

No evidence was obtained of the formation of a 1 : 1-compound.

Silver Iodide and Thiourea.

Silver iodide is not nearly so soluble in hot alcoholic solution of thiourea as the bromide or chloride. The iodide is speedily whitened by thiourea, as in the case of the bromide, and forms a clotted mass, very little of which dissolves. Hence, in a large experiment, the iodide precipitated from 17 grams of nitrate was added gradually to a boiling alcoholic solution of 30·4 grams of thiourea. At first solution took place, but only an inconsiderable proportion of the iodide ultimately dissolved; the liquid was then filtered and allowed to stand for three days, when a white, crystalline precipitate was obtained, which was washed with alcohol and dried for analysis:—

I. 0·5748 gram gave 0·4205 AgI for Ag.
II. 0·3947 „ 0·2875 AgI for I.
III. 0·409 „ 0·1362 Ag reduced by H.

These numbers indicated that the compound was CSN_2H_4,AgI in a partially purified condition, but further washing led to decomposition.

	Theory.	Experiment. I.	Experiment. II.	Experiment. III.
Ag.........	34·70	33·61	—	33·31
I	40·83	—	39·34	—

It may be that the compound $(CSN_2H_4)_2,AgI$ exists in the hot solution, but that decomposition takes place on cooling, resulting in the separation of the 1 : 1-product, retaining a small proportion of the compound richer in thiourea; but in none of the experiments has a substance been obtained which even approached the 1 : 2-compound in composition, though Mr. Werner, who rendered much assistance in this work, spared no trouble in attempts to prepare such a compound in the solid state.

Silver Cyanide and Thiourea.

Silver cyanide, recently precipitated from 17 grams of the nitrate, was treated, as in the other cases, with warm alcoholic solution of

30·4 grams of thiourea. The cyanide dissolved completely, but the solution had to be cautiously evaporated at a low temperature before small crystals separated. The crop was collected, washed with alcohol, and dried at a low temperature, as they decomposed in the steam-bath. The perfectly dry crystals discolour at 115° and afford a black liquid at 126° (sharply).

0·7695 gram gave 0·29 of Ag.
0·4360 ,, 0·717 of $BaSO_4$.

These data agree with the formula $(CSN_2H_4)_2AgCN$.

	Theory.	Experiment.
Ag..........	37·70	37·68
S............	22·37	22·60

In this instance, as in that of silver chloride, a 1 : 1-compound has not been obtained.

All the foregoing substances agree in readily affording silver sulphide when heated to a few degrees beyond the respective melting points, or even before melting, as in the case of the silver cyanide compound just described. Moreover, treatment with weak alkalis tends to cause change in the same direction, just as the action of an alkali easily separates mercaptan from the compound of thiourea with ethyl bromide and iodide. In the latter, the alkyl group is attached to sulphur, and the silver haloïd compounds of thiourea are probably similar in structure.

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XXI.—*A Pure Fermentation of Mannitol and Dulcitol.*

By Percy F. Frankland, Ph.D., B.Sc., F.R.S., and Wm. Frew, F.C.S.

We have in previous communications shown that dulcitol offers far more resistance to fermentation than does its isomer mannitol; thus the former is attacked neither by the *Bacillus ethaceticus* ("On a Pure Fermentation of Mannite and Glycerin," by P. F. Frankland and J. Fox, *Proc. Roy. Soc.*, **46**, 345), nor by the well-known *Pneumococcus* of Friedländer, which readily ferments mannitol (P. F. Frankland, Frew, and Stanley, Trans., 1891, **59**, 253). In fact, as far as we are aware, no fermentative decomposition of dulcitol has hitherto been submitted to careful examination. The only recorded fermentation of dulcitol was obtained by Berthelot with putrid cheese (*Ann. Chim. Phys.* [3], **50**, 348), the products being alcohol butyric acid, and lactic acid.

The organism endowed with the power of fermenting dulcitol we were fortunate enough to discover by accident in a solution of ferric ammonium citrate, prepared for photographic purposes, and which, after standing for a period of 4—6 weeks, was in such a vigorous state of fermentation that it had caused the expulsion of the cork from the bottle which contained it. From this fermenting liquid, inoculations were made into sterile solutions of glucose,[*] and of calcium citrate, in both of which media[†] fermentation was established. Sterile dulcitol tubes were inoculated from the fermenting glucose solution, and, on soon exhibiting vigorous fermentation, were submitted to gelatin-plate cultivation. From the resulting colonies similar dulcitol tubes were inoculated, but in no case did fermentation ensue. Thinking that the fermentative power of the organism had possibly been weakened through cultivation on gelatin, we adopted a method which our experience had shown to be successful in reviving this power, and which consisted in inoculating from the colony into tubes containing sterile dulcitol solution to which 10 per cent. of peptone broth had been added to increase the nutritive value of the liquid. These *dulcitol broth* tubes inoculated from colonies entered into vigorous fermentation, and on inoculating from these into tubes containing ordinary dulcitol solution, the latter was induced to ferment also. The greater facility with which the mannitol is fermentable was exhibited by the fact that inoculations from colonies into ordinary mannitol solution caused the fermentation of the latter without the intervention of a culture in *mannitol broth.* From these dulcitol and mannitol solutions, the fermentation, the purity of which was guaranteed through the organisms tracing their descent from a single

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[*]

Glucose	30 grams	diluted to 1000 c.c. with distilled water.
Peptone	1 ,,	
Salt solution	100 c.c.	

The solutions which we employ for fermentation are made up on the above type; thus the calcium citrate solution referred to would have 30 grams of this salt per litre instead of the glucose. The salt solution mentioned consists of—

Potassium phosphate...........	5·00 grams	diluted to 5000 c.c. with distilled water.
Magnesium sulphate (cryst.)	1·00 ,,	
Calcium chloride (fused)	0·50 ,,	

[†] We have not yet determined whether the calcium citrate was fermented by the same organism as that which causes the fermentation of the dulcitol and mannitol, which is the subject of the present communication.

colony on the gelatin plate, was propagated indefinitely from tube to tube. The morphological characters of the microorganism inducing the fermentations in question are described in the Appendix by Mrs. Percy Frankland.

FERMENTATIONS OF DULCITOL AND MANNITOL. SERIES I.

Two flasks of rather more than 1 litre capacity received the following solutions respectively :—

Dulcitol.

Dulcitol	15·00 grams	diluted with distilled water to 750 c.c.
Peptone	0·75 ,,	
Calcium carbonate....	7·5 ,,	
Salt solution	75 c.c.	

Mannitol.

Mannitol............	15·00 grams	diluted with distilled water to 750 c.c.
Peptone	0·75 ,,	
Calcium carbonate....	7·5 ,,	
Salt solution	75 c.c.	

These flasks containing the liquid were plugged with sterile cotton-wool, and sterilised in the ordinary way by steaming for one hour on three successive days. Both liquids were then inoculated from one and the same pure culture (in dulcitol solution) of nine days age and in vigorous fermentation. They were then placed in the incubator maintained at a temperature of about 38°. The dulcitol flask commenced fermenting on the following, and the mannitol flask on the second, day after inoculation. In both cases, the fermentation was practically finished on the 37th day, but the dulcitol recommenced again faintly on the 44th day, and both flasks were removed from the incubator and submitted to examination on the 49th day.

Examination of Dulcitol Fermentation Products.—The fermented liquid was distilled down until a few drops of the distillate gave no iodoform reaction (Lieben). The alcoholic distillate was then oxidised with potassium dichromate and sulphuric acid, and the excess of oxidising agent subsequently reduced by zinc and sulphuric acid, after which the volatile acids produced were distilled and converted into barium salts as already described (Trans., 1891, **59**, 81). The barium salts dried at 130° amounted to 10·6670 grams, of which 0·589 gram yielded 0·5375 gram $BaSO_4$ or 91·26 per cent., pure barium acetate, yielding 91·37 per cent. $BaSO_4$.

The 10·6670 grams of barium salt are thus equivalent to 3·849 *grams of ethyl alcohol.*

After the alcohol had been distilled off as above, the residue was treated with normal hydrochloric acid, of which 150 c.c. were required to neutralise the 7·5 grams of calcium carbonate originally placed in the flask. 125 c.c. were in the first instance added, and the volatile acids distilled off, and converted into barium salts in the usual way. The following fractions, dried at 130°, were obtained :—

Fraction I, 0·9483 gram of barium salt.

0·3735 gram yielded 0·3375 gram $BaSO_4$ = 90·36 per cent.
0·2875 ,, ,, 0·2595 ,, ,, = 90·26 ,,

Fraction II, 0·5675 gram of barium salt.

0·185 gram yielded 0·16775 gram $BaSO_4$ = 90·68 per cent.
0·267 ,, ,, 0·24225 ,, ,, = 90·73 ,,

35 c.c. of the normal acid were now added, and the following fraction obtained :—

Fraction III, 0·542 gram of barium salt, yielding 0·4935 gram $BaSO_4$ = 91·05 per cent.

The total amount of barium salts was thus 2·0578 grams, and as, from the above analyses, it is seen to consist almost exclusively of acetate, it may be taken as equivalent to 0·9684 *gram of acetic acid.*

The liquid left after distilling off the volatile acids contained, as usual in these fermentations, a small amount of brown, flocculent, insoluble matter, which, when dried at 105°, weighed 0·1710 gram. The filtrate from this was repeatedly shaken out with ether (no less than 40 times), and, on evaporation, this yielded 0·973 gram of residue, which was nearly pure succinic acid melting at 179°.

After extracting with ether as above, there was further recovered from the liquid some material insoluble in alcohol, and weighing 0·5939 gram (dried at 100°). This was found to consist of calcium succinate (representing the succinic acid which had failed to be extracted with ether), and corresponds to 0·4022 gram of succinic acid, so that the total amount of the latter found was 0·9730 + 0·4022 = 1·3752 grams.

After removing the calcium with the calculated amount of sulphuric acid, and getting rid of the hydrochloric acid, there remained only 1·67 grams of residue. Its limited amount and the partial decomposition which it had undergone prevented its more detailed examination. It is, however, obvious that the fermentation was complete or nearly so, as otherwise the unaltered dulcitol would have been obtained here.

Examination of Mannitol Fermentation Products.—The examination of these products was carried out in the same manner as for the dulcitol above.

The alcohol distillate, on oxidation, yielded 9·6865 grams of barium salt, which, on analysis, proved to be pure barium acetate, since 0·6850 gram of the salt, dried at 130°, gave 0·6242 gram $BaSO_4$ = 91·12 per cent., the theory for barium acetate being 91·37 per cent. $BaSO_4$.

These 9·6865 grams of barium acetate are equivalent to 3·495 grams of ethyl alcohol.

In the distillation of the volatile acids, the following fractions of barium salts were obtained:—

Fraction I consisted of 2·340 grams of barium salt, dried at 130°, of which:—

I. 0·4578 gram yielded 0·4165 gram $BaSO_4$ = 90·98 per cent.
II. 0·4155 „ „ 0·3780 „ „ = 90·97 „

Fraction II consisted of 1·7472 grams of barium salt dried at 130°, of which:—

I. 0·3370 gram yielded 0·3070 gram $BaSO_4$ = 91·10 per cent.
II. 0·2325 „ 0·2120 „ „ = 91·18 „

Fraction III consisted of 0·10825 gram of barium salt, dried at 130°, which yielded 0·0955 gram $BaSO_4$ = 88·22 per cent.

The first two fractions were thus practically pure acetate, whilst the third very small fraction was somewhat impure, as is generally the case at the end of the distillation for volatile acids. The total amount of barium salts, 4·19545 grams, may thus be taken as equivalent to 1·9743 gram of acetic acid.

After removal of the volatile acids, there was obtained, as usual, some brown, flocculent organic matter insoluble in hydrochloric acid, and amounting to 0·0870 gram (dried at 100—105°).

In the extraction with ether (which was repeated no less than 40 times), there was obtained 1·858 grams of succinic acid melting at 180°, whilst 0·4285 gram of calcium succinate, equivalent to 0·2906 gram of succinic acid, was subsequently recovered from the solution by precipitation with alcohol. Thus, in all, 1·8580 + 0·2906 = 2·1486 grams of succinic acid were obtained.

Finally, after removal of the calcium chloride by precipitating with a calculated amount of sulphuric acid in alcoholic solution, a residue weighing 1·44 gram was left, the nature of which could not be ascertained.

The results obtained in the two fermentations may be thus summarised:—

	15 grams Dulcitol yielded	15 grams Mannitol yielded
Ethyl alcohol	3·849 grams	3·495 grams.
Acetic acid	0·9684 ,,	1·9743 ,,
Succinic acid	1·3752 ,,	2·1486 ,,
Residue left after fermentation ...	1·67 ,,	1·44 ,,

or the following molecular proportions:—

C_2H_6O	0·0837	0·0760
$C_2H_4O_2$	0·01614	0·0329
$C_4H_6O_4$	0·0117	0·0182

FERMENTATION OF DULCITOL AND MANNITOL. SERIES II.

Having, in the first series of experiments, ascertained the principal products to which this fermentation gives rise, we, in the next instance, arranged the experiments so that the gaseous products could be also examined. For this purpose the fermentations were carried on in bottles provided with corks and delivery tubes opening under mercury (as described in "Fermentations induced by the *Pneumococcus* of Friedländer," Trans., 1891, **59**, 260).

The fermentations of both dulcitol and mannitol were conducted in duplicate. The four bottles were charged as follows:—

	Dulcitol I.	Dulcitol II.
Dulcitol.........	8·0 grams.	8·0 grams.
Peptone.........	0·4 ,,	0·4 ,,
Calcium carbonate	4·0 ,,	4·0 ,,
Salt solution	40 c.c.	40 c.c.
	Diluted with distilled water to 400 c.c.	Diluted with distilled water to 400 c.c.

	Mannitol I.	Mannitol II.
Mannitol	8·6 grams	8·0 grams
Peptone	0·43 ,,	0·4 ,,
Calcium carbonate	4·3 ,,	4·0 ,,
Salt solution	43 c.c.	40 c.c.
	Diluted with distilled water to 430 c.c.	Diluted with distilled water to 400 c.c.

These four solutions were all inoculated with the same pure culture of the organism, a cultivation in dulcitol solution of five days age and in a vigorous state of fermentation at the time. The bottles commenced fermenting on the third day after inoculation.

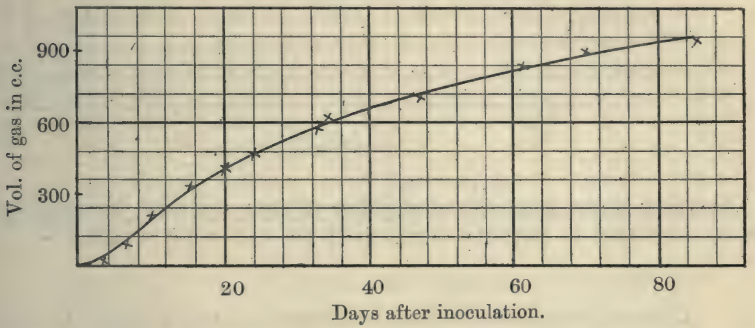
The Fermentation Gases.—We will, in the first instance, take into consideration the volume and composition of the gases evolved in the four fermentations. In these experiments we endeavoured to maintain the level of mercury in the pneumatic trough constant, so that the pressure under which the fermentations took place should be as uniform as possible. The volume of the gases evolved was measured, and in each case reduced to 0° and 760 mm.

Volume of Gas evolved in Fermentation.

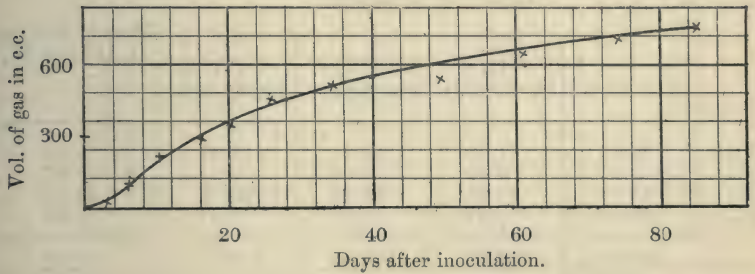
Days after inoculation.	Total gas in c.c.			
	Dulcitol I.	Dulcitol II.	Mannitol I.	Mannitol II.
3	36·6	34·0	38·8	28·8
5	—	—	—	134·5
6	107·6	101·4	142·8	159·6
9	—	—	—	258·5
10	209·1	192·7	244·1	—
13	—	—	—	377·6
14	—	—	—	400·3
15	312·8	—	342·4	—
16	—	284·1	—	—
18	—	—	—	500·3
20	389·8	346·6	—	—
22	—	—	461·2	—
24	478·5	—	—	—
26	—	440·3	—	—
27	—	—	544·2	586·9
30	—	—	657·4	—
33	595·2	—	—	—
34	621·9	506·2	740·6	—
38	—	—	776·8	—
39	—	—	801·5	—
40	—	—	820·9	—
41	—	—	834·7	687·8
47	714·0	—	—	—
50	—	531·0	956·9	—
57	—	—	1077·4	—
61	817·5	648·6	—	799·2
64	—	—	1169·6	—
73	894·4	720·9	1273·8	873·4
80	—	—	1367·4	—
85	951·1	746·7	1418·7	933·3

From the above it will be seen that the evolution of gas continued over a period of 85 days from the date of inoculation, and that whilst the volumes given off from the solutions Dulcitol I, Dulcitol II, and Mannitol II were approximately equal, that from Mannitol I was very considerably in excess, even after making due allowance for the fact that in the latter 8·6 grams of mannitol were employed, whilst in the other three experiments only 8 grams of mannitol and dulcitol respectively were used. Thus, reducing the volume of gas from Mannitol I in the proportion of 8·6 : 8·0, we still have 1319·7 c.c., which is a much larger volume than was obtained in the other three experiments. The evolution of gas in these four parallel experiments is most conveniently followed by means of the accompanying diagrams, in which the ordinates represent volume of gas, and the abscissæ lapse of time after inoculation.

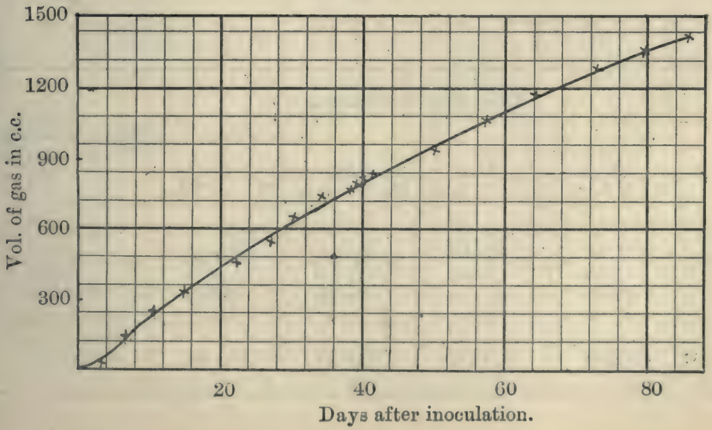
DULCITOL I.



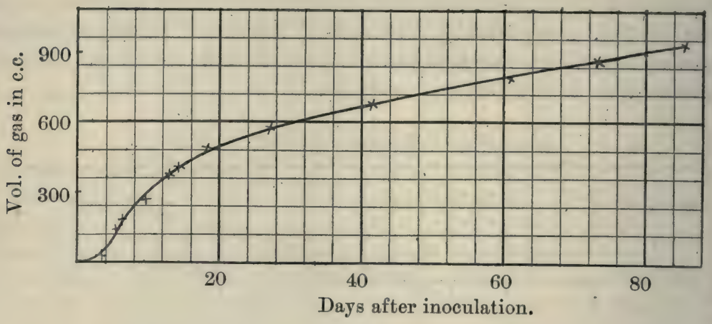
DULCITOL II.



MANNITOL I.



MANNITOL II.



Samples of the gas evolved at different stages of each fermentation were submitted to careful analysis with the following results:—

Composition of Gas Evolved in Fermentation of Dulcitol I.

	Days after inoculation.				Mean of Analyses II, III, and IV.
	I. 2—5 days.	II. 14—19 days.	III. 33—46 days.	IV. 72—84 days.	
CO_2 ..	26·94	51·19	56·81	59·84	55·95
O....	0·50	0·09	0·00	0·14	0·07
H....	44·56	48·25	43·04	39·78	43·69
N....	28·00	0·47	0·15	0·24	0·29
	100·00	100·00	100·00	100·00	100·00

Composition of Gas Evolved in Fermentation of Dulcitol II.

	Days after inoculation.				Mean of Analyses II, III, and IV.
	I. 2—5 days.	II. 15—19 days.	III. 33—49 days.	IV. 72—84 days.	
CO_2 ..	27·93	52·16	54·85	50·87	52·63
O....	0·24	0·08	0·07	—	0·08
H....	45·75	47·59	44·92	49·13	47·21
N....	26·08	0·17	0·16	—	0·08
	100·00	100·00	100·00	100·00	100·00

Composition of Gas Evolved in Fermentation of Mannitol I.

	Days after inoculation.							Mean of Analyses II—VII.
	I. 2—5 days.	II. 9—14 days.	III. 26—29 days.	IV. 37—38 days.	V. 39—40 days.	VI. 40—49 days.	VII. 72—79 days.	
CO_2	33·78	56·50	57·95	56·02	55·30	52·46	53·91	55·36
O ..	0·02	0·25	0·22	0·08	0·33	0·05	—	0·16
H ..	52·93	42·94	41·76	43·79	44·20	47·24	46·09	44·34
N ..	13·27	0·31	0·07	0·11	0·17	0·25	—	0·14
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

Composition of Gas Evolved in Fermentation of Mannitol II.

	Days after inoculation.				Mean of Analyses II—IV.
	I. 4—5 days.	II. 12—13 days.	III. 26—40 days.	IV. 72—84 days.	
CO_2 ..	44·69	55·74	62·38	60·75	59·63
O	0·00	0·04	—	—	0·01
H	54·37	44·10	37·62	39·25	40·32
N	0·94	0·12	—	—	0·04
	100·00	100·00	100·00	100·00	100·00

From these analyses, it will be seen that the composition of the gases in Mannitol I and in the two dulcitol fermentations is very similar, whilst in the case of Mannitol II there is a decided excess of carbonic anhydride, and a deficiency of hydrogen, as compared with the others. A further reference to these differences will be made later on (see p. 270).

In the next place, it becomes necessary to determine the quantities of carbonic anhydride and hydrogen evolved in each of the fermentations. This can, of course, be only approximately done, as we are not acquainted with the composition of the gas at every stage of the fermentation, but only at intervals. We have, therefore, in each case taken the mean of the analyses, neglecting only the first one of each series, as in these there was invariably some residual air from the fermenting bottle. Calculating, then, the total volume in each case as of the composition indicated by the average of the analyses, we obtain the following results :—

			CO_2.	H.
Dulcitol I ..	951·1 c.c.,	containing	532·1 c.c.	415·5 c.c.
,, ..	,,	,,	1·0489 gram	0·0372 gram.
Dulcitol II ..	746·7 c.c.	,,	393·0 c.c.	352·5 c.c.
,, ..	,,	,,	0·7747 gram	0·0316 gram.
Mannitol I ..	1418·7 c.c.	,,	785·4 c.c.	629·1 c.c.
,, ..	,,	,,	1·5482 gram	0·0564 gram.
Mannitol II ..	933·3 c.c.	,,	556·5 c.c.	376·3 c.c.
,, ..	,,	,,	1·0970 gram	0·0337 gram.

As the methods employed in the examination of the fermented liquids were in the main similar to those described above, it will be only necessary to mention any points of departure from them.

Dulcitol I.—The *alcohol* distillate gave on oxidation, &c.,

> 2·8015 grams of barium salts, dried at 130°, of which 0·601 gram yielded 0·5473 gram $BaSO_4$ = 91·06 per cent. $BaSO_4$. These barium salts, therefore, correspond to 1·011 *gram of ethyl alcohol.*

The *volatile acids* gave 1·000 gram of barium salt, dried at 130°, of which

0·2058 gram yielded 0·19525 gram $BaSO_4$ = 94·87 per cent.
0·1700 ,, 0·16150 ,, = 95·00 ,,
Mean .... 94·94 ,,

These barium salts, therefore, correspond to

0·1284 *gram formic acid*
0·3215 ,, *acetic* ,,

By subsequent extraction with ether (in which we made use of the very convenient continuous apparatus of Schwarz for the extraction of liquids, described under "Extraction" in *Thorpe's Dictionary of Applied Chemistry*, p. 96), there was obtained 0·264 *gram of succinic acid* melting at 178°.

Dulcitol II similarly gave

> 2·2175 grams of barium salts, dried at 130°, of which 0·3748 gram yielded 0·3415 gram $BaSO_4$ = 91·11 per cent. $BaSO_4$, thus corresponding to 0·800 *gram of ethyl alcohol.*

The volatile acids gave 0·7825 gram of barium salt dried at 130°, of which

0·1762 gram yielded 0·1660 gram $BaSO_4$ = 94·21 per cent.
0·1945 „ 0·1830 „ = 94·09 „

Mean .... 94·15 „

corresponding to

0·078 *gram of formic acid*,
0·277 „ *acetic* „

0·1715 gram of succinic acid melting at 180° was similarly obtained.

After extracting with ether as above, the liquids from Dulcitol I and II were evaporated to dryness, and the residues found to be crystalline and free from gummy matter. These residues were, in the first instance, extracted with alcohol (about 93 per cent.), made strongly acid with hydrochloric acid to liberate any traces of succinic acid which might be present as calcium succinate, and subsequently washed with alcohol to rid the insoluble residue of hydrochloric acid. The residue, which was a white powder, was dried at 100° and weighed. The alcoholic filtrate also deposited some more of this white powder. Of this white residue, nearly insoluble in alcohol, there were obtained from

Dulcitol I, 7·3695 grams.

On analysis, it yielded the following results :—

I. 0·3083 gram gave 0·0565 gram CaO = 13·10 per cent. Ca.
II. 0·2475 „ 0·2327 „ AgCl = 23·31 „ Cl.
III. 0·1713 gram, on combustion with lead chromate in a closed tube, gave 0·083 gram OH_2 and 0·1548 gram CO_2 = 5·37 per cent. H and 24·64 per cent. C.

Dulcitol II, 8·7755 grams.

On analysis, this yielded the following results :—

I. 0·3935 gram gave 0·0760 gram CaO = 13·80 per cent. Ca.
II. 0·3590 „ 0·0687 „ = 13·68 „ Ca.
III. 0·2670 „ 0·2597 gram AgCl = 24·12 „ Cl.
IV. 0·3180 „ 0·3085 „ = 24·06 „ Cl.
V. 0·3060 „ on combustion with CuO, 0·1337 gram OH_2 and 0·2665 gram CO_2 = 4·86 per cent. H and 23·76 per cent. C. (In this combustion the carbon was certainly low, as a minute quantity was visible in the boat at the end, and could not be burnt off.)
VI. 0·213 gram, on combustion with chromate of lead in a closed tube, gave 0·101 gram OH_2 and 0·1907 gram CO_2 = 5·26 per cent. H and 24·41 per cent. C.

The above analytical figures of both these dulcitol residues correspond very closely with the theoretical for a molecular compound of dulcitol and calcium chloride:—

	Dulcitol Residue I.	Dulcitol Residue II.		
	I.	I.	II.	$C_6H_{14}O_6,CaCl_2$.
C	24·64	23·76	24·41	24·57
H....	5·37	4·86	5·26	4·78
O	33·58	33·46	32·59	32·77
Ca ...	13·10	13·80	13·68	13·65
Cl....	23·31	24·12	24·06	24·23
	100·00	100·00	100·00	100·00

That the calcium chloride in these residues is not present in the free state is clearly shown by the fact that these residues are not deliquescent. The compound appears to be decomposed by water, for, on dissolving in water and adding a large excess of alcohol, a substance crystallised out which was practically free from calcium and chlorine, and which was presumably pure dulcitol.

The compound of dulcitol and calcium chloride was obtained pure by extraction in a Soxhlet tube with alcohol for many days, and the white, minutely crystalline substance separating from the alcohol was dried at 100°, and the chlorine determined with the following result:—

I. 0·1802 gram substance taken yielded 0·1759 gram AgCl, corresponding to 24·24 per cent. Cl.

II. 0·1487 gram substance taken yielded 0·1465 gram AgCl, corresponding to 24·44 per cent. Cl.

Similarly, on combustion with chromate of lead, figures for carbon and hydrogen were obtained closely harmonising with those required for the compound $C_6H_{14}O_6,CaCl_2$:—

I. 0·2365 gram substance yielded 0·2152 gram CO_2 and 0·1075 gram H_2O, corresponding to C 24·82 per cent., and H 5·05 per cent.

II. 0·2312 gram substance yielded 0·2107 gram CO_2 and 0·1033 gram H_2O, corresponding to C 24·85 per cent., and H 4·97 per cent.

From the above analytical figures, it can be calculated that the Dulcitol Residue I contained 4·69 grams, and the Dulcitol Residue II 5·46 grams, of unaltered dulcitol, thus:—

	Dulcitol Residue I. (7·3695 grams.)	Dulcitol Residue II. (8·7755 grams.)
Ca	13·10	13·74
Cl..........	23·31	24·09
Dulcitol	63·59 = 4·69 grams.	62·17 = 5·46 grams.
	100·00	100·00

From this, it will be seen that less than half of the dulcitol employed had been decomposed by fermentation; we therefore examined this residual dulcitol with the polarimeter, thinking that possibly ordinary dulcitol, which is inactive, might be composed of equal molecules of oppositely active dulcitols, and that one of these would have been attacked in the fermentation to the exclusion of the other. *A 10 per cent. solution of this residual dulcitol compound, however, proved to be quite inactive.*

In the alcoholic liquid obtained in extracting the above dulcitol residue, there was further finally found a quantity of organic matter (doubtless dulcitol for the most part) which amounted to 0·6935 gram in the case of Dulcitol I, and 0·5825 gram in that of Dulcitol II.

We must now turn to the examination of the fermented mannitol solutions.

Mannitol I.

The *alcohol* distillate gave, on oxidation, 3·6105 grams of barium salts, dried at 130°, of which 0·5125 gram yielded 0·4668 gram $BaSO_4$ = 91·08 per cent. $BaSO_4$.

This barium salt is, therefore, barium acetate, and corresponds to 1·3026 *gram of ethyl alcohol.*

The *volatile acids* gave 0·9885 gram of barium salts, dried at 130°, of which

0·18475 gram yielded 0·1735 gram $BaSO_4$ = 93·91 per cent.
0·20600 „ 0·1935 „ = 93·93 „

Mean .... 93·92 „

The barium salts are thus equivalent to

Formic acid, 0·091 gram,
Acetic „ 0·360 „

or 0·479 gram calculated as acetic acid.

Succinic acid was obtained by the ether extraction apparatus (see p. 264) to the amount of 0·172 gram, melting at 182°. A further quantity of succinic acid, amounting to 0·2468 gram, was obtained as below, making the total amount recovered from this fermentation 0·4188 *gram.*

Mannitol II.

Similarly 2·859 grams of barium salts were obtained, of which 0·5265 gram gave 0·4795 gram $BaSO_4$ = 91·07 per cent. $BaSO_4$. This barium salt is thus equivalent to 1·0315 *gram of ethyl alcohol.* The *volatile acids* gave 1·3035 gram of barium salts, of which

0·1633 gram yielded	0·1582 gram $BaSO_4$	= 96·88	per cent.
0·1942 ,,	0·1885 ,,	= 97·07	,,
	Mean	96·98	,,

which corresponds to a mixture of

Formic acid, 0·263 gram,
Acetic ,, 0·308 ,,

or to 0·651 gram calculated as acetic acid.

Of *succinic acid*, there was similarly obtained 0·1987 gram, melting at 179°. The further quantity of succinic acid, obtained as below, amounted to 0·092 gram, making a total on the whole fermentation of 0·2907 *gram.*

After extracting with ether, as above, there was a small quantity of a calcium salt insoluble in alcohol, which appeared to be calcium succinate, and of this

Mannitol I yielded 0·3638 gram of this calcium succinate = 0·2468 gram of succinic acid.

Mannitol II yielded 0·1360 gram of this calcium succinate = 0·902 gram of succinic acid.

These quantities of succinic acid have, therefore, been added to those obtained by ether extraction mentioned above.

The alcoholic filtrate from the calcium succinate above was distilled to free it from alcohol, and then potassium carbonate was added slightly in excess of the amount required to completely precipitate all the calcium. The calcium carbonate thus precipitated was filtered off, the filtrate evaporated, dried at 100°, and weighed. This residue would consist of potassium chloride, potassium carbonate, and any residual mannitol or other organic matter not determined. These residues weighed respectively for

Mannitol I, 11·8093 grams.

0·2628 gram of this residue gave, on ignition with sulphuric acid, 0·18825 gram K_2SO_4 = 32·11 per cent. K in the residue.

Again, 0·28545 gram gave 0·323 gram AgCl = 28·06 per cent. Cl in the residue.

The chlorine found requires only 30·83 per cent. K, so that the remaining 1·28 per cent. K must be calculated to K_2CO_3,OH_2. Thus, the residue has the following composition:—

KCl................	58·89
K_2CO_3,H_2O	2·56
Residual mannitol, &c. (by difference)	38·55 = 4·552 grams residual mannitol.
	100·00

Mannitol II, 11·4785 grams.

0·2455 gram of this gave 0·1667 gram K_2SO_4 = 30·43 per cent. K in the residue.

Again, 0·2688 gram gave 0·2883 gram AgCl = 26·60 per cent. Cl.

The chlorine found requires only 29·22 per cent. K, so that the excess of 1·21 per cent. K must be calculated to K_2CO_3,H_2O, thus:—

KCl	55·82
K_2CO_3,H_2O	2·42
Residual mannitol, &c. (by difference)	41·76 = 4·793 grams residual mannitol.
	100·00

Collecting the results of these four fermentations (two dulcitol and two mannitol), we have

	Dulcitol.		Mannitol.	
	I.	II.	I.	II.
	grams	grams	grams	grams
Substance employed	8·0	8·0	8·6	8·0
Ethyl alcohol..........	1·011	0·800	1·3026	1·0315
Formic acid	0·1284	0·078	0·091	0·263
Acetic acid............	0·3215	0·277	0·360	0·308
Succinic acid	0·264	0·1715	0·4188	0·2907
Carbonic anhydride	1·0489	0·7747	1·5482	1·0970
Hydrogen.............	0·0372	0·0316	0·0564	0·0337
Residual substance	5·3835	6·0425	4·552	4·793
Substance fermented....	2·6165	1·9575	4·0480	3·2070

In considering the above results, it must be borne in mind that a part of the carbonic anhydride found is derived from the decomposition of the calcium carbonate by the formic, acetic, and succinic acids set free in the fermentation. The amount of carbonic anhydride from this source can be calculated from the quantities of these acids which were determined, and which are recorded in the above summary, thus:—

	Dulcitol.		Mannitol.	
	I.	II.	I.	II.
	grams	grams	grams	grams
CO_2 due to formic acid..	0·0614	0·0373	0·0435	0·1258
,, acetic ,, ..	0·1179	0·1016	0·1320	0·1129
,, succinic acid	0·0984	0·0640	0·1562	0·1084
Total CO_2 due to secondary decomposition of $CaCO_3$	0·2777	0·2029	0·3317	0·3471
CO_2 due to fermentation	0·7712	0·5718	1·2165	0·7499
H : CO_2 (fermentation)	:: 1 : 20·73	18·09	21·57	22·25
Acetic acid : alcohol	:: 1 : 3·14	2·89	3·62	3·35
	acetic acid : alcohol 1 mol. : 4 mols.		acetic acid : alcohol 2 mols. : 9 mols.	
	3·07		3·45	

On subtracting the carbonic anhydride due to decomposition of calcium carbonate from the total carbonic anhydride obtained, the remainder is obviously that having its origin in the fermentative decomposition itself, as indicated above. Now the proportion in which this fermentation carbonic anhydride stands to the hydrogen evolved approximates, in the case of the two dulcitol fermentations, and is practically identical, in the case of the two mannitol fermentations, to CO_2 : H :: 22 : 1, which is the proportion of equal molecules,

$$\begin{array}{l} CO_2 : H_2 = 22 : 1 \\ \;\;44 \quad\;\; 2 \end{array}$$

which is also the proportion of carbonic anhydride to hydrogen in formic acid:—$CH_2O_2 = CO_2 + H_2$.

Thus, the whole evolution of gas in the fermentation may be referred to a preliminary production of formic acid, which, subsequently undergoing decomposition, gives rise to carbonic anhydride and hydrogen, in equal volumes. That this view is not a mere theory, but based upon experimental evidence, is shown by the fact that, in the above fermentations, a variable proportion of the formic acid in question has actually escaped decomposition, and so we have, as it were, been able to lay hands both on the primary product, that is, formic acid, and also on the secondary products, carbonic anhydride and hydrogen. Moreover, it is evident that conducting the fermentations in a closed space, as in the case of these gas-bottle experiments, tends to prevent the decomposition of the formic acid. Thus, in the fermentation conducted in flasks plugged with cotton wool (see pp. 256, 257), there was practically no formic acid found on analysis, the whole of the volatile acid being acetic acid. We have, moreover, found the same difference in the case of fermentations conducted with the *Bacillus ethaceticus* and with Friedländer's *Pneumococcus;* when these fermentations were carried on in flasks plugged with cotton wool, there was little or no formic acid discoverable, whilst, when the same fermentations were made to take place in bottles with delivery tubes dipping into a mercury bath, there was in every case an abundance of formic along with the acetic acid.

Whether the retardation in the formic acid decomposition is due to the effect of the complete absence of oxygen on the organism, or to the higher pressure under which the fermentation takes place in consequence of the delivery tubes dipping under mercury in the gas experiments, we are at present unable to say, as this point must be made the subject of further investigation.

As regards the relationship existing between the other products of these fermentations, it will be seen—

1. *That the formic acid and alcohol are produced in the proportion of an equal number of molecules.* Thus, adding the hydrogen and carbonic anhydride (excluding that due to the decomposition of calcium carbonate) to the formic acid obtained as such, we have in the four fermentations:—

	Dulcitol.		Mannitol.	
	I.	II.	I.	II.
	grams	grams	grams	grams
H_2	0·0372	0·0316	0·0564	0·0337
CO_2	0·7712	0·5718	1·2165	0·7499
CH_2O_2................	0·1284	0·0780	0·0910	0·2630
Total	0·9368	0·6814	1·3639	1·0466
C_2H_6O...............	1·0110	0·8000	1·3026	1·0315

Thus, the weights of formic acid and alcohol produced are approximately equal, and since their molecular weights are also equal, $CH_2O_2 = 46$, $C_2H_6O = 46$, they are present in molecular proportion.

The greatest discrepancy occurs in the case of the fermentation

Dulcitol II, in which we have already seen that the proportion of $CO_2 : H_2$ also departed most from that of 22 : 1 by weight. The determination of carbonic anhydride in these experiments is necessarily attended with inaccuracy in consequence of its solubility, whilst the hydrogen determinations are entitled to be regarded as more accurate, both because of its insolubility, and also on account of the large volume corresponding to a given weight. Now, if we take the hydrogen figures as the basis of our calculations, the above relationship is still more conspicuous. Thus, if, instead of taking for carbonic anhydride the actual weights obtained, we take the weights of hydrogen multiplied by 22, we have:—

	Dulcitol.		Mannitol.	
	I.	II.	I.	II.
	grams	grams	grams	grams
H_2	0·0372	0·0316	0·0564	0·0337
$CO_2 = (H_2 \times 22)$......	0·8184	0·6952	1·2408	0·7414
CH_2O_2	0·1284	0·0780	0·0910	0·2630
Total............	0·9840	0·8048	1·3882	1·0381
C_2H_6O...............	1·0110	0·8000	1·3026	1·0315

2. The proportion of acetic acid to alcohol, is less constant being for

Dulcitol.		Mannitol.	
I.	II.	I.	II.
1 : 3·14	1 : 2·89	1 : 3·62	1 : 3·35

These relationships correspond, however, approximately to 1 mol. of acetic acid to 4 mols. of alcohol in the case of the dulcitol fermentations—

$$\begin{array}{ccc} C_2H_4O_2 & : & 4C_2H_6O \\ (60) & & 4(46) \\ 1 & : & 3{\cdot}07 \end{array}$$

Whilst the relationship in the case of the mannitol fermentations approximates more closely to that subsisting between 2 mols. of acetic acid and 9 mols. of alcohol—

$$\begin{array}{ccc} 2C_2H_4O_2 & : & 9C_2H_6O \\ 2(60) & & 9(46) \\ 120 & & 414 \\ 1 & : & 3{\cdot}45 \end{array}$$

3. The relationship between the succinic acid and the other products is more difficult to ascertain, as the error on the quantitative determination of such a small absolute amount of this substance is probably considerable.

It would, however, appear that the succinic acid is formed in the proportion of 1 mol. to 2 mols. of acetic acid. Thus the molecular weight of succinic acid (118) is almost exactly twice that of acetic acid (60), and the quantities of succinic acid found are just about equal to those of acetic acid, the average amount of succinic acid found in the four fermentations being 0·2863 gram, and that of the acetic acid 0·3166 gram.

We may explain the formation of the above products in the proportions indicated by assuming that the fermentative decomposition of the dulcitol and mannitol takes place in the following manner:—

1. 1 mol. of dulcitol or mannitol breaks up into 2 mols. of ethyl alcohol, 1 mol. of carbonic anhydride, and 1 mol. of formic acid:—

$$C_6H_{14}O_6 = 2C_2H_6O + CO_2 + CH_2O_2.$$

2. 1 mol. of dulcitol or mannitol breaks up into 1 mol. of succinic acid, 1 mol. of acetic acid, and 2 mols. of hydrogen:—

$$C_6H_{14}O_6 = C_4H_6O_4 + C_2H_4O_2 + 2H_2.$$

Now, if 2 mols. of the dulcitol or mannitol break up accordiug to Equation 1, and 1 mol. according to Equation 2, we shall have

$$\underset{\substack{\text{Dulcitol or}\\ \text{mannitol.}}}{3C_6H_{14}O_6} = \underset{\substack{\text{Ethyl}\\ \text{alcohol.}}}{4C_2H_6O} + 2CO_2 + \underset{\substack{\text{Formic}\\ \text{acid.}}}{2CH_2O_2} + \underset{\substack{\text{Succinic}\\ \text{acid.}}}{C_4H_6O_4} + \underset{\substack{\text{Acetic}\\ \text{acid.}}}{C_2H_4O_2} + 2H_2,$$

corresponding in all but one point to the analytical results which we have obtained above. Thus, all the products discovered by analysis are represented; moreover, there are 4 mols. of alcohol to 1 of acetic acid; the hydrogen and carbonic anhydride are present in molecular proportion (2 of each), that is, in the proportion in which they are present in formic acid, and this carbonic anhydride and hydrogen, together with the 2 mols. of formic acid, are in all equivalent to 4 mols. of formic acid, or the same number of molecules as there are of alcohol. In all these points, the equation is in precise accord with the results of actual analysis, whilst it is only in the matter of the succinic acid that there is any discrepancy; for, according to the equation, the succinic acid and acetic acid should be formed in molecular proportion, whilst analytically, only about one half of this amount of succinic acid was actually obtained. As already pointed out, however, the accurate determination of succinic acid is surrounded with difficulties, and it is quite possible that the amount actually found may be considerably below the truth. This is, however, a matter for subsequent investigation, and we would provisionally suggest the above reactions as the simplest explanation of the fermentative phenomena observed.

It will be seen that only a small, but variable, proportion of the formic acid produced in the first instance escapes decomposition into carbonic anhydride and hydrogen, for in none of the fermentations, either of the dulcitol or of the mannitol, does the formic acid actually found amount to more than a small fraction of the alcohol.

The principal results at which we have arrived in this investigation may be summarised as follows:—

1. Dulcitol and mannitol are similarly fermented by the organism in question, the products being ethyl alcohol, acetic and succinic acids, hydrogen, and carbonic anhydride.

2. When the gaseous products are permitted to freely diffuse into the air through a cotton-wool stopper, the fermentation is a complete one lasting about five or six weeks, but when the fermentation is carried on in a closed space, without admission of air, the evolved gases being collected over mercury, then a large proportion, upwards of 50 per cent., of the dulcitol or mannitol remains unfermented, and amongst the products there are found, in addition to those mentioned above, considerable quantities of formic acid. We have also observed the production of formic acid in similar closed fermentations with the *Bacillus ethaceticus* and with Friedländer's *Pneumococcus.*

3. The carbonic anhydride and hydrogen evolved are, after deducting the carbonic anhydride due to the decomposition of carbonate of lime by the acids mentioned, approximately in molecular proportion, or in that in which they are present in formic acid, and owing to the variable quantities in which the formic acid was discovered in the several fermentations, it is only reasonable to suppose that more or less of the formic acid at first produced had been decomposed with evolution of an equal number of molecules of carbonic anhydride and hydrogen. This is the more probable, as in each of the fermentations the sum of the formic acid, hydrogen, and carbonic anhydride approximately corresponds in molecules of formic acid to the amount of alcohol in molecules produced in the same fermentation.

4. The decomposition of the dulcitol and mannitol may be regarded as taking place in two independent reactions:—

$$(a.)\ C_6H_{14}O_6 = 2C_2H_6O + CO_2 + CH_2O_2,$$
$$(b.)\ C_6H_{14}O_6 = C_4H_6O_4 + C_2H_4O_2 + 2H_2,$$

but, from the proportion which the acetic acid bears to the alcohol, it appears that 2 mols. are decomposed according to Equation *a* for every one that is decomposed according to *b*; thus:—

$$3C_6H_{14}O_6 = 4C_2H_6O + C_2H_4O_2 + C_4H_6O_4 + CH_2O_2 + 2CO_2 + 2H_2$$

indicates the proportions in which the several products were approximately obtained in each of the fermentations, the only marked discrepancy being in the case of the succinic acid, the amount of which was only about half that demanded by the above, but this deficiency may not improbably be due to the difficulty attending the accurate determination of succinic acid in such mixtures.

5. In recovering the unaltered dulcitol from the fermentation products, we have incidentally discovered a compound of dulcitol with calcium chloride of the composition $C_6H_{14}O_6,CaCl_2$. This compound is soluble in water with decomposition, but very insoluble in alcohol, from which, however, it can be crystallised unchanged.

6. In view of the products to which this organism gives rise, we would provisionally propose for it the name of *Bacillus ethacetosuccinicus.*

7. The fermentation induced by this organism differs fundamentally from that resulting from the *Bacillus ethaceticus* and from Friedländer's *Pneumococcus*, previously described by one of us, in that with it a much larger quantity of succinic acid is formed, whilst neither of the others has the power of fermenting dulcitol.

APPENDIX.

Morphological Characterisation of the Micro-organism causing Fermentation.

By GRACE C. FRANKLAND.

ON submitting any of the fermenting solutions to plate cultivation with gelatin-peptone, there are formed, in the course of two to three days, colonies which are of very variable appearance, according as they are situated in the depth or on the surface of the gelatin film. The depth colonies are yellowish in colour, with smooth contour, and mostly of an oval form. When the colony reaches the surface, it forms a small pin-head, from which there extends a very thin and highly irregular expansion with slightly serrated edge. This expansion exhibits slight iridescence, and in plates on which there are only few colonies it may have a diameter of as much as half an inch. The surface colonies have not, however, in all cases this thin expansion surrounding them, but, on the contrary, are not unfrequently sharply circumscribed, thicker, less transparent, much more shining, and of regularly circular contour, much resembling, in fact, a small drop of milk. In case this diversity of appearance should be due to the presence of several organisms, mannitol and dulcitol tubes were inoculated from each of the three types of colony described above, and in all cases these tubes entered into fermentation. These fermenting tubes were again submitted to plate cultivation, and in each case all three types of colony made their appearance on each plate, thus conclusively proving that one and the same organism gives rise to these several types of colony; in fact, in some instances one and the same colony exhibited both the features in question, that is to say, it was of the "milk drop" type on one side and of the "irregular expansion" type on the other. When the plates are very much crowded, all the surface colonies are of the "milk drop" type, the expansions only occurring on sparsely populated plates. Indeed, each colony evidently militates against the extension of its neighbours even at considerable distances, a phenomenon which I have frequently observed in the case of the plate cultures of other organisms. This influence at a distance is apparently caused through the products elaborated by the organisms extending over some considerable area outside the actual colonies themselves, as is indicated by the fact that the entire plate often presents a somewhat fluorescent appearance. The same phenomenon may be very strikingly observed in the case of plate cultures of the well-known *Bacillus pyocyaneus.*

Examined with a low power (1 inch), the depth colonies are seen to have a smooth rim but somewhat irregular contour, as represented in the plate, Fig. 1. The contents are finely granular and of a brownish colour. The surface expansion colonies, when similarly examined, are seen to consist of very finely granular contents arranged in characteristic, wavy lines, more especially towards the margin, as is shown in Fig. 2. The centre of the colony is always dark, indicating the nucleus from which the expansion has proceeded.

The annexed photographs serve to illustrate the appearance of the plate cultures:—

No. 1, a crowded plate culture, obtained from a fermenting dulcitol broth tube. In this, all the surface colonies are of the "milk drop" type, and devoid of irregular expansions.

No. 2, a less crowded plate culture from the same source, showing the "milk drop" colonies, in most cases giving rise to small, irregular expansions.

No. 3, a plate culture from another fermenting dulcitol broth tube, also showing the "surface expansion," "milk drop," and small depth colonies.

Inoculated into agar-agar, and kept at the ordinary temperature, a thick growth rapidly forms in the depth around the track of the needle, whilst the surface becomes covered with a white growth, which soon extends downwards into the medium to the depth of about $\frac{1}{8}$ inch.

Journ. Chem. Soc April 1892.

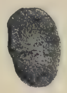


Fig. 1.

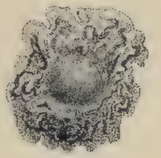


Fig. 2.

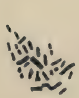


Fig. 3.

HARRISON & SONS, LITH. ST MARTINS LANE, W.C.

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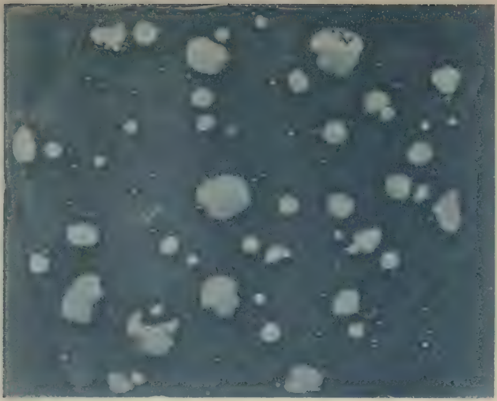

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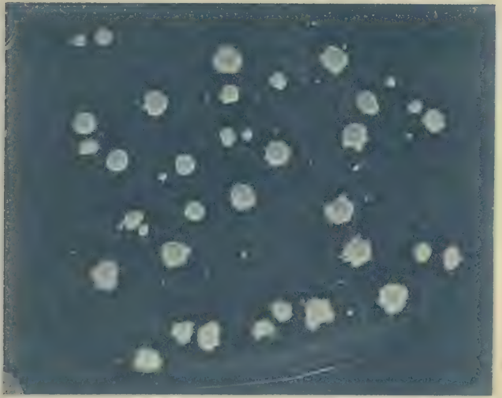

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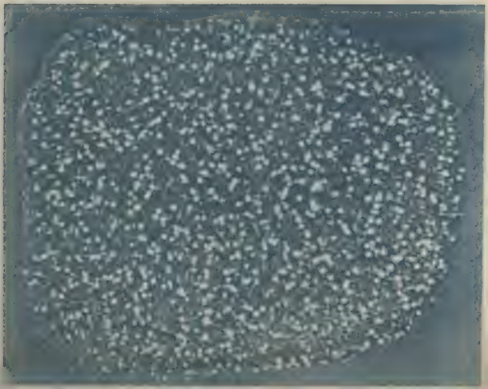


No. 1.

In broth, and kept at the ordinary temperature, it renders the liquid turbid, and a white deposit forms, whilst, after a few weeks, a white film appears on the surface of the liquid.

On potatoes, at the ordinary temperature, the growth is rapid, extending broadly over the surface, and at first only distinguishable from the potato itself by its thickened and irregular edge, but, on keeping, it becomes dark-brown.

Inoculated into gelatin peptone, it produces a thin, iridescent growth with a very irregular edge which extends over the surface. This extension of the growth would seem to depend upon the dry or moist condition of the gelatin, for in the former it restricts itself, the growth being at the same time thicker, to the needle streak across the surface, and only later gradually expands on either side of it.

In the depth, the track of the needle is marked by a slight beaded appearance.

On microscopic examination with a high power ($\frac{1}{12}$ inch), the organism, as taken from a gelatin-plate culture, is seen to be a small bacillus of variable dimensions both as to thickness and length, but on an average it is 1·7—2·5 μ in length by 0·5—1·0 μ in width, generally occurring in pairs, and not unfrequently the transverse divisions between the bacilli are obliterated, which gives rise to the appearance of short threads. The appearance of the bacilli is also very similar when examined from the fermenting solutions, only fewer threads were generally observable. In no case were spores found, even very old potato cultivations exhibiting no appearance resembling them. Examined in "drop cultures" under the microscope, the bacilli are seen to possess a vibratory motion only, and do not travel across the field.

Fig. 3 of plate represents the appearance of the bacilli as taken from a surface colony on a gelatin plate after four days' growth.

XXII.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. XXIII. *The Isomeric α-Bromocinnamic Acids.*

By S. Ruhemann, Ph.D., M.A., University Lecturer in Organic Chemistry.

The two isomeric bromocinnamic acids, which are formed from αβ-dibromhydrocinnamic acid by the action of alcoholic potash, have been frequently subjected to investigation since their discovery by Glaser (*Annalen,* **143**, 325). It was the fact observed by this chemist that the acid, which was regarded by him as the β-bromo-derivative, changes into the α-acid when distilled or boiled with fuming hydriodic acid, which especially claimed the attention of chemists. A. Michael and G. M. Browne (*Ber.*, **19**, 1378) were the first to find that both these isomeric bromo-acids must be regarded as α-derivatives of cinnamic acid, inasmuch as they prepared the true β-bromocinnamic acid from phenylpropiolic acid by the addition of hydrogen bromide. This result was supported by E. Erlenmeyer's observation that both acids got from dibromhydrocinnamic acid yield benzaldehyde on oxidation by potassium permanganate (*Ber.*, **23**, 3130). Glaser's β-bromocinnamic acid is, therefore, also an α-substitution product, and it is called by Michael allo-α-cinnamic acid, and by Erlenmeyer α-bromisocinnamic acid, since it yields isocinnamic acid on displacement of the bromine by hydrogen (*loc. cit.*). Both α-bromo-substitution products bear the same relation to one another that fumaric acid does to maleïc acid; they are stereoisomerides. As maleïc acid can be transformed into fumaric acid by hydriodic acid, so, as Glaser found, may allo-α-(α-iso-)bromocinnamic acid be changed into the α-acid by the same reagent. As maleïc acid, on treatment in alcoholic solution with hydrogen chloride, yields ethyl fumarate, so is, according to Barisch (*J. pr. Chem.* [2], **20**, 184), allo-α-bromocinnamic acid transformed into the ethereal salt of its stereoisomeride under analogous conditions.

Some years ago, the two α-bromo-acids were studied by Anschütz and Selden (*Ber.*, **20**, 1383); they found that under the influence of phosphorus pentachloride the bromo-derivative of isocinnamic acid yields α-bromocinnamyl chloride, and this, when submitted to the action of ammonia and of aniline, yielded the amide and the anilide of this acid.

I have undertaken the further study of these two acids with the view of investigating the action of ammonia, and especially of phenylhydrazine, on their ethereal salts.

The ethyl salts, which were prepared by the action of ethyl iodide on the silver salts, show a remarkable difference in their behaviour towards ammonia. Ethyl α-bromocinnamate, when allowed to remain in contact with a strong aqueous solution of this reagent for 24 hours, is transformed into a mass of crystals. The melting point, 119°, of the substance after recrystallisation from water, and a nitrogen determination, show that it is α-bromocinnamide, which Anschütz and Selden (*loc. cit.*) obtained from α-bromocinnamyl chloride:—

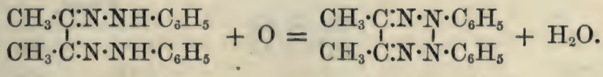
	Calculated for $C_9H_8BrNO_2$.	Found.
N	6·19 per cent.	6·32 per cent.

The ammoniacal mother liquor from the product of the reaction contains the ammonium salt of the α-bromo-acid; for, after concentration, hydrochloric acid separates from it the acid melting at 131°.

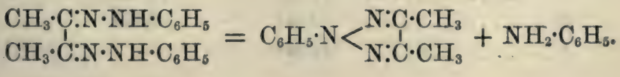
The ethereal salt of α-bromisocinnamic acid, however, reacts very slowly with ammonia. After standing for weeks with a strong aqueous solution of the reagent, only a very small quantity of crystals appeared. These, removed from the unaltered oil, were dissolved in boiling water, and, on cooling, crystallised out in colourless needles melting at 128—129°. The substance is, no doubt, α-bromisocinnamide, but the amount which was formed was not sufficient for verification by analysis. The ammoniacal filtrate on concentration deposits the sparingly soluble ammonium α-bromocinnamate, from which hydrochloric acid sets free the acid melting at 120°.

Action of Phenylhydrazine on the Ethereal Salts of the α-Bromocinnamic Acids.

I was led to the investigation of the action of phenylhydrazine on the ethyl salts of the two α-bromocinnamic acids through v. Pechmann's researches on the osazones (*Ber.*, **21**, 2751; *Annalen*, **262**, 265). He showed that on oxidation the phenylosazones of 1:2-diketo-compounds yield osotetrazones, and are transformed into triazole derivatives with elimination of aniline. These reactions of diacetylosazone find their expression in the following equations:—

(1.)


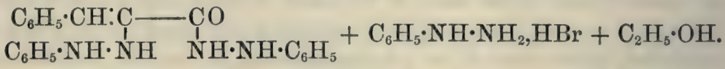
$$\begin{matrix} CH_3\cdot C\colon N\cdot NH\cdot C_3H_5 \\ | \\ CH_3\cdot C\colon N\cdot NH\cdot C_6H_5 \end{matrix} + O = \begin{matrix} CH_3\cdot C\colon N\cdot N\cdot C_6H_5 \\ |\qquad\quad | \\ CH_3\cdot C\colon N\cdot N\cdot C_6H_5 \end{matrix} + H_2O.$$

(2.)


$$\begin{matrix} CH_3\cdot C\colon N\cdot NH\cdot C_6H_5 \\ | \\ CH_3\cdot C\colon N\cdot NH\cdot C_6H_5 \end{matrix} = C_6H_5\cdot N{<}\begin{matrix} N\colon C\cdot CH_3 \\ | \\ N\colon C\cdot CH_3 \end{matrix} + NH_2\cdot C_6H_5.$$

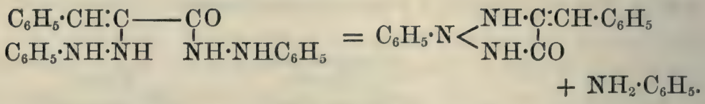
Their formation from compounds which contain two phenylhydrazine groups in their molecules rendered it probable that the α-bromocinnamic acids would, after introduction of two phenylhydrazine residues, give rise to a substance which may be formed according to the equations:—

(1.) $C_6H_5{\cdot}CH{:}CBr{\cdot}COOC_2H_5 + 3C_6H_5{\cdot}NH{\cdot}NH_2 =$



$$\begin{array}{ll} C_6H_5{\cdot}CH{:}C\text{——} & CO \\ \quad\mid & \mid \\ C_6H_5{\cdot}NH{\cdot}NH & NH{\cdot}NH{\cdot}C_6H_5 \end{array} + C_6H_5{\cdot}NH{\cdot}NH_2{,}HBr + C_2H_5{\cdot}OH.$$

(2.)



$$\begin{array}{ll} C_6H_5{\cdot}CH{:}C\text{——} & CO \\ \quad\mid & \mid \\ C_6H_5{\cdot}NH{\cdot}NH & NH{\cdot}NHC_6H_5 \end{array} = C_6H_5{\cdot}N{<}\begin{array}{l} NH{\cdot}C{:}CH{\cdot}C_6H_5 \\ \quad\mid \\ NH{\cdot}CO \end{array} + NH_2{\cdot}C_6H_5.$$

This would be a derivative of a compound which stands in the same relation to tetrahydrotriazole as pyrrazole to pyrrazolone.

The action of phenylhydrazine on the ethereal salts of the α-bromocinnamic acids is very violent; it is, therefore, advisable to use only small quantities of the salts at a time. The operation was conducted in the following manner:—5 grams of ethyl α-bromisocinnamate was mixed with about 8 grams of phenylhydrazine, and the mixture digested in a flask till the reaction just began. The liquid became deep red, and, with considerable rise of temperature, a rapid evolution of gas set in, which was sometimes so violent that the whole frothed over. Among the products given off, nitrogen, ammonia, carbonic anhydride, and benzene were noticed. The reaction was allowed to continue without further warming, and the contents of the flask, when cold, were agitated with dilute hydrochloric acid. On collecting the semi-solid red substance which remained undissolved, and washing it first with water and then with alcohol, a red, crystalline powder was left on the filter. This substance was soluble with difficulty in boiling alcohol, and, on cooling, came down in orange needles, which, after two crystallisations, were quite pure and melted at 172°. The compound, on analysis, gave the following numbers, which correspond to the formula $C_{15}H_{11}N_3O$:—

I. 0·1125 gram substance gave 0·0490 gram H_2O and 0·2975 gram CO_2.

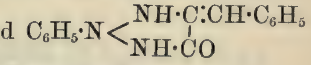
II. 0·1204 gram substance yielded 17·6 c.c. of moist nitrogen measured at 18° and 757 mm. bar.

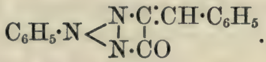
	Theory for $C_{15}H_{11}N_3O$.	Found. I.	Found. II.
C	72·29	72·12	—
H	4·41	4·80	—
N	16·86	—	16·81

The molecular weight of this substance was determined by Raoult's method, using benzene as the solvent, with the following result:—

Weight of substance	0·3815 gram.
" benzene	35·8105 grams.
Melting point of the benzene	5°
" " the mixture	4·8°
Depression of the melting point.	0·2°
Molecular weight derived from the above data.......................	261
Theory for $C_{15}H_{11}N_3O$	249

This compound is soluble with great difficulty in boiling alcohol, but readily in glacial acetic acid, more so in chloroform and benzene. The same compound is formed on treating the ethyl salt of the isomeric bromo-acid with phenylhydrazine in the same manner; the reaction, however, requires a somewhat higher temperature, and it is less violent than in the former case.

The mode of formation of the substance melting at 172° from the ethyl salts of the two α-bromocinnamic acids may be interpreted in the manner stated above, but the compound  $C_6H_5{\cdot}N<\begin{array}{l}NH{\cdot}C{:}CH{\cdot}C_6H_5\\NH{\cdot}CO\end{array}$ is not the final product of the reaction; it is oxidised to



$$C_6H_5{\cdot}N<\begin{array}{l}N{\cdot}C{:}CH{\cdot}C_6H_5\\N{\cdot}CO\end{array}.$$

This oxidation is undoubtedly effected by the phenylhydrazine, which is thus reduced to aniline and ammonia. The substance may be called benzylidenetriazolone, or perhaps, more correctly, cinnamylphenylazimide. This constitution is supported also by the facts that the compound is neutral to mineral acids and bases, and does not react with acetic anhydride or with nitrous acid.

As it seemed difficult to stop the reaction at its various stages, and to isolate the different compounds, I prepared one of these intermediate products, the hydrazide of α-bromocinnamic acid, and transformed it into the azimide.

The phenylhydrazide of α-bromocinnamic acid is readily obtained from the hydrazine and the acid chloride, the latter being formed by the action of phosphorus pentachloride on α- or allo-α-bromocinnamic acids (Anschütz and Selden, *loc. cit.*). In order to moderate the violent reaction which took place on mixing phenylhydrazine with the bromocinnamyl chloride, the latter was diluted with ether. After removal of the ether a coloured product remained, which was washed with dilute hydrochloric acid, and recrystallised from alcohol, using animal charcoal for decolorisation. The hot alcoholic solution, on cooling, deposited almost colourless needles which melted at 120°, and gave on analysis the following numbers:—

I. 0·2058 gram substance gave 15·4 c.c. moist nitrogen, measured at 16° and 774 mm.

II. 0·2915 gram substance yielded, by Carius' method, 0·1706 gram AgBr.

	Calculated for $C_{15}H_{13}N_2BrO$.	Found.	
		I.	II.
N	8·83	8·88	—
Br	25·20	—	24·90

The phenylhydrazide, $C_6H_5 \cdot CH \colon CBr \cdot CO \cdot NH \cdot NH \cdot C_6H_5$, is readily soluble in alcohol and in ether, and, on digesting with excess of phenylhydrazine, yields cinnamylphenylazimide, which was identified by its melting point (172°) and chemical behaviour.

Formation of Cinnamylphenylazimide from Ethyl Dibromhydrocinnamate.

As the mode of preparing the ethereal salts of the α-bromocinnamic acids above described involves rather troublesome operations, and is, moreover, accompanied by a considerable loss, I was led to use the ethereal salt of αβ-dibromhydrocinnamic acid for the preparation of cinnamylphenylazimide. The splitting off of hydrogen bromide from this salt takes place, as I found, even in the cold, when it is allowed to remain in contact with strong aqueous ammonia for some time. The salt is thus transformed into the amide of α-bromocinnamic acid, which was identified by the crystalline form and the melting point, 119°. Ethyl dibromhydrocinnamate cannot easily be prepared from the acid by the action of hydrogen chloride on its alcoholic solution, as only part of it is transformed into the salt, the larger portion remaining unchanged. It is, however, readily formed by adding the calculated quantity of bromine to ethyl cinnamate dissolved in chloroform; after removal of the solvent, it solidifies on cooling, and is sufficiently pure for the following reaction. The ethereal salt is quickly heated with phenylhydrazine in quantities of 2 grams of the one to 4 grams of the other. The organic salt first enters into solution, then crystals separate, which are, no doubt, phenylhydrazine hydrobromide, and finally a violent evolution of gas takes place. The reaction was allowed to continue, and the semi-solid product, when cold, treated in the manner stated before for the purification of cinnamylphenylazimide from the α-bromocinnamic acids. The substance, after recrystallisation from boiling alcohol, is identical with that got from the monobromo-acids; for it melts at the same temperature, and gave on analysis the following numbers :—

I. 0·1410 gram substance gave 0·0605 gram H_2O and 0·3760 gram CO_2.
II. 0·1365 gram substance gave 0·0590 gram H_2O and 0·3610 gram CO_2.
III. 0·1720 gram substance yielded 24·2 c.c. moist nitrogen measured at 12° and 764 mm.

	Theory. $C_{15}H_{11}N_3O$.	Fouud. I.	 II.	 III.
C........	72·29	72·70	72·13	—
H........	4·41	4·67	4·70	—
N........	16·86	—	—	16·78

The yield of cinnamylphenylazimide which is obtained either from the α-bromocinnamic acids or from αβ-dibromhydrocinnamic acid, is only small, amounting to 10—15 per cent. There is formed, however, along with this substance another which is of some interest.

Imide of Dicinnamylphenylazimide.

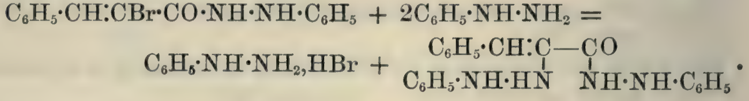
If the product of the reaction of phenylhydrazine on the ethereal salts of these acids be agitated with dilute hydrochloric acid, and the acid filtrate from the compound melting at 172° be allowed to stand for some time in an open vessel, or if a current of air be passed through the heated solution, it becomes cloudy, and deposits a flocculent, red precipitate. On collecting this, washing it with water, and crystallising from hot, glacial, acetic acid, red needles, melting at 248°, are obtained. On analysis, it gave numbers which agree with the formula $C_{24}H_{18}N_4O_2$:—

I. 0·1540 gram substance gave 0·0640 gram H_2O and 0·4140 gram CO_2.
II. 0·1015 gram substance gave 12·2 c.c. moist nitrogen measured at 16° and 756 mm.

	Theory. $C_{24}H_{18}N_4O_2$.	Found. I.	 II.
C..........	73·10	73·10	—
H..........	4·57	4·61	—
N..........	14·21	—	13·93

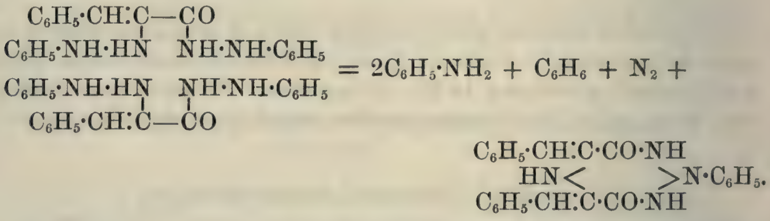
It is soluble with difficulty in boiling glacial acetic acid, but very readily in hot benzene, petroleum, and acetone.

The mode of formation of this substance from the ethereal salts of the bromo-acids and phenylhydrazine may be explained as follows:—The base converts the organic salts first into the phenylhydrazide of α-bromocinnamic acid, which then reacts with phenylhydrazine according to the equation



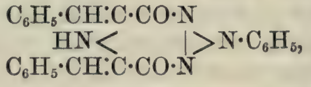
$$C_6H_5\cdot CH{:}CBr\cdot CO\cdot NH\cdot NH\cdot C_6H_5 + 2C_6H_5\cdot NH\cdot NH_2 = C_6H_5\cdot NH\cdot NH_2,HBr + \begin{array}{l} \quad C_6H_5\cdot CH{:}C - CO \\ C_6H_5\cdot NH\cdot HN \quad NH\cdot NH\cdot C_6H_5 \end{array}.$$

The latter compound in a further stage of the reaction then undergoes two different changes; part of it yields cinnamylphenylazimide with elimination of aniline and subsequent oxidation, whilst another part of the hydrazilhydrazine condenses most likely in the manner indicated by the equation



$$\begin{array}{l} \quad C_6H_5\cdot CH{:}C - CO \\ C_6H_5\cdot NH\cdot HN \quad NH\cdot NH\cdot C_6H_5 \\ C_6H_5\cdot NH\cdot HN \quad NH\cdot NH\cdot C_6H_5 \\ \quad C_6H_5\cdot CH{:}C - CO \end{array} = 2C_6H_5\cdot NH_2 + C_6H_6 + N_2 + HN\!<\!\begin{array}{l} C_6H_5\cdot CH{:}C\cdot CO\cdot NH \\ C_6H_5\cdot CH{:}C\cdot CO\cdot NH \end{array}\!>\!N\cdot C_6H_5.$$

The latter compound is probably contained in the acid filtrate from cinnamylphenylazimide, and oxidises to the imide of dicinnamylphenylazimide,



$$HN\!<\!\begin{array}{l} C_6H_5\cdot CH{:}C\cdot CO\cdot N \\ C_6H_5\cdot CH{:}C\cdot CO\cdot N \end{array}\!\Big|\!>\!N\cdot C_6H_5,$$

under the influence of the oxygen of the air. The same substance may be obtained directly from cinnamylphenylazimide, and this formation supports the view with regard to its constitution expressed above.

Reduction of Cinnamylphenylazimide.

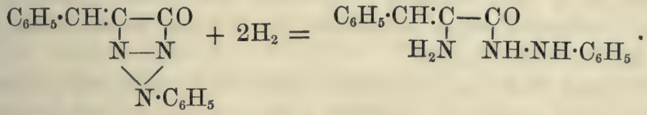
Cinnamylphenylazimide yields a colourless solution when boiled in the presence of alcohol with tin and hydrochloric acid on a water-bath in a flask connected with a reflux condenser. The clear liquid is poured off from the metal, and the tin removed from the solution by hydrogen sulphide. The colourless filtrate from the sulphide of tin, when evaporated in a dish, deposits a flocculent, red precipitate gradually increasing in quantity. This substance is the imide of dicinnamylphenylazimide, for when crystallised from glacial acetic acid it melts at 248°, and on analysis gives numbers corresponding to the formula $C_{24}H_{18}N_4O_2$:—

I. 0·125 gram substance gave 0·055 gram H_2O and 0·336 gram CO_2.
II. 0·133 gram substance gave 0·0545 gram H_2O and 0·357 gram CO_2.
III. 0·1505 gram substance yielded 18·4 c.c. moist nitrogen measured at 11° and 746 mm.

	Theory.	Found.		
	$C_{24}H_{18}N_4O_2$.	I.	II.	III.
C	73·10	73·30	73·20	—
H	4·57	4·92	4·55	—
N	14·21	—	—	14·34

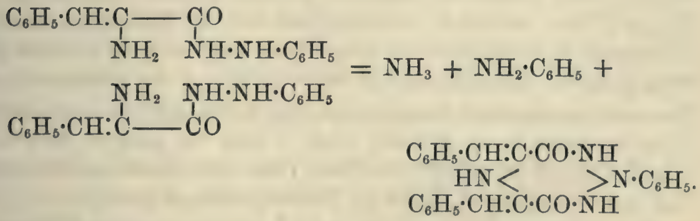
The original filtrate from this substance evolves ammonia on the addition of potash, and gives the aniline test with a solution of bleaching powder. These facts throw a light on the formation of the imide of dicinnamylphenylazimide, and allow of the interpretation of the reaction expressed in the following equations :—

(1.)



$$\begin{array}{l}C_6H_5\cdot CH{:}C-CO\\ \qquad\quad N-N\\ \qquad\quad\ \diagdown\diagup\\ \qquad\quad N\cdot C_6H_5\end{array} + 2H_2 = \begin{array}{l}C_6H_5\cdot CH{:}C-CO\\ \qquad\quad H_2N\quad NH\cdot NH\cdot C_6H_5\end{array}.$$

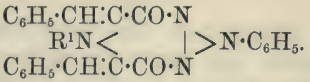
(2.)



$$\begin{array}{l}C_6H_5\cdot CH{:}C——CO\\ \qquad\quad NH_2\quad NH\cdot NH\cdot C_6H_5\\ \qquad\quad NH_2\quad NH\cdot NH\cdot C_6H_5\\ C_6H_5\cdot CH{:}C——CO\end{array} = NH_3 + NH_2\cdot C_6H_5 + \begin{array}{l}C_6H_5\cdot CH{:}C\cdot CO\cdot NH\\ \qquad HN< \qquad >N\cdot C_6H_5.\\ C_6H_5\cdot CH{:}C\cdot CO\cdot NH\end{array}$$

This compound is to be regarded as the final product of the reduction, and yields the azimide under the influence of the oxygen of the air. I have attempted to isolate the hydrazimido-compound from the solution freed from tin, by evaporating it in a current of hydrogen sulphide, and extracting the product with ether. A substance was indeed taken up by this solvent, and, on distilling off the ether, remained behind as a brown, tarry mass, which did not appear inviting for further study.

The imide of dicinnamylphenylazimide, as mentioned before, dissolves in glacial acetic acid, benzene, chloroform, and acetone; the solutions are red. The behaviour with alcohol is interesting. On adding alcohol to a trace of the substance contained in a test-tube, the spirit becomes purple even in the cold; this colour deepens on boiling, and disappears on the addition of an acid. This phenomenon can only be due to the solvent action of alcohol on the glass, and indicates that the compound has acid properties. Indeed a few drops of an alkali or an alkali carbonate dissolve the imido-compound, when suspended in alcohol, with a deep violet colour, and on evaporating the solution, a dark-blue substance with metallic lustre remains behind, which is the salt of the cinnamic acid derivative. This is very soluble in alcohol, and is readily decomposed by acids, which deposit the imide of dicinnamylphenylazimide unchanged. The property of this compound to form salts can only be attributed to the acid character of the imido-group, and their constitution is to be expressed by the general formula:—



$$\begin{array}{l} C_6H_5\cdot CH{:}C\cdot CO\cdot N \\ \qquad R^1N< \qquad\quad | >N\cdot C_6H_5. \\ C_6H_5\cdot CH{:}C\cdot CO\cdot N \end{array}$$

The alkali salts are very soluble in alcohol with violet colour, but gradually dissociate when boiled with water. The ammonium salt especially is very unstable; the violet ammoniacal solution of the imido-compound, when evaporated to dryness, decomposes, leaving the red substance behind.

The fact that this compound reacts so readily with alkalis, and yields violet solutions, makes it a most sensitive indicator. A few drops of the coloured solution produced by boiling a trace of the substance with alcohol in a test-tube may be used for this purpose. The point of neutralisation is well marked, if for volumetric analysis the acid is run into the alkali to which the indicator has been added. The indicator is so delicate that it may be used to determine the small amount of alkali dissolved from the glass, and to investigate the solvent action of spirit on different sorts of glass.

In conclusion, I may add that I intend to study the action of phenylhydrazine on the ethereal salts of other αβ-dibromo-acids, particularly of those belonging to the fatty series.

XXIII.—*On the Refractive Power of certain Organic Compounds at Different Temperatures.*

By W. H. PERKIN, Ph.D., F.R.S.

FROM the study of magnetic rotations at widely different temperatures it has been found that they are not absolutely constant, but fluctuate to a slight extent, becoming smaller as the temperature rises and larger as it falls; the amount of variation, generally speaking, being greatest in cases where the rotation is large; and, as it has been pointed out (Trans., 1889, **55**, 750) that there is usually an analogy between the peculiarities of magnetic rotations and the refraction of light, it was thought desirable to see if it also existed in reference to changes of temperature.

Dale and Gladstone, in 1863, came to the conclusion that $\frac{\mu-1}{d}$ was constant, or nearly so, for all temperatures, and the small variations which had been observed when working at different temperatures were considered by Landolt and others as arising from experimental errors. But Nasini and Bernheimer, in 1885 (*Gazzetta*, **15**, 59), show from the results of their examination of the refractive power of a number of aromatic substances, that slightly smaller numbers are obtained at higher than at lower temperatures; and this difference they do not consider to be due to experimental errors. Kettler (*Ann. Phys. Chem.*, 1888, **33**, 506 and 662) has also examined water, alcohol and carbon bisulphide; and from his results the same discrepancy is found to occur, so that $\frac{\mu-1}{d}$ does not appear to be constant for all temperatures. The object of the following experiments, however, was not only in reference to this, but also to see if the alterations due to changes of temperature varied with different classes of substances, as they do in the case of the magnetic rotation.

To make experiments of this kind, special apparatus is necessary, so that the prisms containing the substance may be maintained at a constant temperature while on the spectrometer. R. Ruhlmann (*Ann. Phys. Chem*, 1867, **132**, 19) gives an account of a prism arranged for the purpose, and later Nasini and Bernheimer (*Gazzetta*, 1885, **15**, 59) also describe an apparatus which is an improvement on this. It may be said to consist of a hollow prism, surrounded by a jacket, except at those parts of the two faces where the light is required to enter and pass out; the temperature being regulated by passing the vapour of some substance of known boiling point, or heated water, through this jacket. Kettler (*Ann. Phys. Chem.*, 1888, **23**, 366) has also described an elaborate refractometer which he used in his experiments.

The apparatus employed in the following measurements is practically an air-bath fitted in the centre of the spectrometer, and consists of a very thick cylindrical copper cell, in which the prism is placed, slots being cut in its sides for the entrance and exit of the light. In the walls, and also in the thick copper lid of this cell, channels are formed, so that steam or water of any desired temperature can be made to circulate through them; and thus it can be cooled or heated as desired. The slots for the admission and exit of light are provided with sliding shutters, by which their apertures may be closed or reduced in size at pleasure. The details of this apparatus will be best understood by reference to the accompanying drawings. Fig. I represents the complete apparatus; Fig. II, a horizontal section through the dotted line on Fig. III; Fig. III, is a vertical section; and Fig. IV, a diagram showing how the water-channels are connected.

Fig. II.—This shows the slots used when measuring the refractive and dispersive power of substances: these are marked *a*, *a*, and are made sufficiently wide so that when the prism is removed light may freely pass through the centre of the cell, as shown by the dotted line; this enables any adjustment of the collimator and telescope to be made without removing the cell from the spectrometer. A third slot, *a'*, is also provided; this is used when measuring the angle of the prism when cold and when heated. *c*, *c*, *c*, *c*, *c* are the sliding shutters for closing or reducing the apertures of the slots, as may be required, and thus preventing any unnecessary change of the temperature of the air in the cell by the entrance of the surrounding air. *b* shows the position of the prism.

Fig. III.—In this vertical section the slots are marked *a*, and the sliding shutters *c*, *c*. *e e* is the copper lid with which the cell is provided, and the aperture in its centre marked *p* is an elongated opening through which the tube ground into the prism, and supporting the thermometer, passes, as seen in Fig. I, *n*, *o*. The principal object of this section is to show the position of the water-passages; these are marked *g g'*, *h h'*, *i i'*, and *l l'*; they were formed in the cell by turning grooves in its side and edges, and in the same manner in the lid. These were afterwards converted into tubes or channels, by soldering pieces of metal over them, or where the surfaces are required to be level by letting them in, as seen in the section. These channels, however, were first interrupted, and then connected vertically, as seen in Fig. IV, their original course being indicated by the dotted lines. About 2 mm. of the bottom of the cell was turned out, so that when

Fig. I.

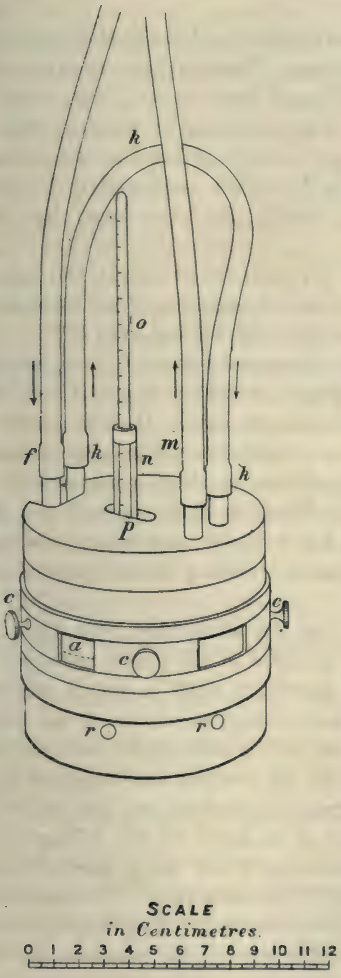


Fig. II.

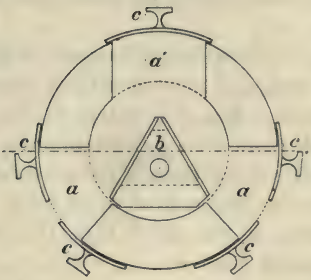


Fig. III.

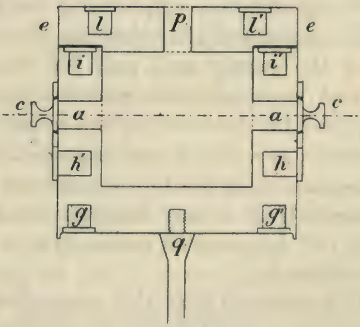
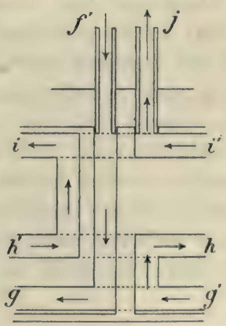


Fig. IV.



standing on the spectrometer it rests on its edges only; thus less conduction of heat takes place, and it also enables it to be turned freely on its centre. A rod, marked *q*, is screwed into the centre of the cell, and passes down the column which supports the spectrometer. The cell is thus kept in its place, and can be turned round to any desired extent.

Fig. IV shows how the water or steam circulates through the channels of the cell, and needs but little description. Passing down the vulcanised tube *f*, Fig. I, it enters f', Fig. IV, and flows on to *g*, then round the cell from g' to *h*, returning to h' on to *i*, and after passing round the cell a third time, it passes away by i', and *j*. After this the water enters the vulcanised tube *k k k*, Fig. I, which conducts it to the channels in the lid *l*, Fig. III, and, finally, it flows away by the vulcanised tube *m*.

When boiling water is circulated through the channels, the temperature of the prism and its contents can be maintained at 92° about, but when steam is employed it can be raised to a little over 97°.

On account of the elasticity of the vulcanised tubes* *f*, *k*, *m*, which form the supply and exit for the water or steam, the cell can be turned on its axis with ease to a much greater extent than is actually required for determining the refractive power of any substance it may contain; *r*, *r*, Fig. I, are two small apertures in which a screw with a non-conducting head of ebonite can be fitted so that the cell can be moved about in any direction when hot without any inconvenience. The cell is provided inside with a small levelling stand supporting the prism.†

It is believed that this apparatus has the advantage over that of Nasini and Bernheimer, inasmuch as all sides of the prism are equally heated. Originally the prism was provided with a small stirrer worked by clockwork, but it has not been found necessary to use this.

To see what influence the rarefied air in the cell would have on the readings, a flat reflector was placed in its centre; the image of the slit was then made to fall upon this from the collimator, the reflected image being viewed with the telescope at an angle of 45°. The angle was first carefully read, and the telescope fixed while the cell was cold; it was then heated up to about 85° for some time. On examination, no shifting of the image could be discovered. This was repeated several times with the same results, different angles being used. It is evident, therefore, that no practical error could arise from this source.

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* A low and somewhat hard quality of vulcanised tubing is found to be more suitable for this apparatus than a good quality, as it keeps more cylindrical when heated, and the passage of water or steam is not impeded.

† This apparatus was made by Hilger.

The hollow glass prism had an angle of about 60°, and no change took place in its angle when heated up to 90°.

The method of using this apparatus is simple. The lid of the cell is first drawn aside, and the prism previously filled with the substance to be examined placed in position. The lid is then replaced, and the tube with the thermometer passed through its elongated opening into the prism, and the interstices filled in with cotton wool. The sliding shutters are then closed, and the water or steam allowed to pass through the channels until the temperature indicated by the thermometer in the prism remains practically constant; they are then opened sufficiently to adjust the prism approximately, and then brought as close to each other as they can be without interfering with the passage of the light. After standing for a little while, the temperature is noted, the prism adjusted, and observations made. The cell is then turned, so that a second set of observations may be repeated from the other side of the prism.

Since bringing the subject before the Society in June last (Proc., 1891, 115), most of the substances there referred to have been remeasured; this has resulted in a revision of the numbers then given. A few fresh substances have also been examined.

The following numbers are in most instances averages of two or more sets of measurements.

As the magnetic rotation has been determined of two of the substances examined by Nasini and Bernheimer at different temperatures, namely, thymol and cinnamic alcohol, the results they obtained are tabulated and introduced into this paper for comparison.

Before proceeding further, it may be useful to remark that in the following tables, the differences given in the columns $\frac{\mu - 1}{d}$ and $\frac{\mu - 1}{d}p$ represent but small differences in the measurements of the angles; this is especially the case with substances of low refractive power; taking water as an example, the difference in the column $\frac{\mu - 1}{d}$ for 68·7° of 0·00130 represents about 0° 4′ 30″, and in the case of the very highly refractive body methylene iodide, in the analogous column for 78·6° of 0·00236 represents about 0° 48′. The results are therefore influenced considerably by small errors in the measurements, and as the densities come into the calculations, any small errors in these have an influence on the final results, which therefore cannot be regarded as exact numbers, though it is hoped they are close approximations.

In the following tables, the differences are first given for the temperatures at which the bodies were examined; they are then given

Water.

$d\frac{15^\circ}{4^\circ}$ 0·99916, $d\frac{73{\cdot}7^\circ}{4^\circ}$ 0·96959.

Line.	μ.			$\frac{\mu-1}{d}$.			$\frac{\mu-1}{d}p$.		
	t.		Difference for 68·7°.	*t.*		Difference for 68·7°.	*t.*		Difference for 68·7°.
	15°.	83·7°.		15°.	83·7°.		15°.	83·7°.	
A..............	1·32943	1·31866	0·01077	0·32971	0·32865	0·00106	5·9348	5·9158	0·0190
C..............	1·33174	1·32065	0·01108	0·33202	0·33071	0·00131	5·9763	5·9527	0·0236
D..............	1·33362	1·32248	0·01113	0·33390	0·33259	0·00131	6·0102	5·9867	0·0235
F..............	1·33758	1·32646	0·01112	0·33787	0·33669	0·00118	6·0806	6·0604	0·0202
Average for D. ...	—	—	0·01102	—	—	0·00121	—	—	0·0216

Difference for 100°.

A..............	0·01568	0·00154	0·0277
C..............	0·01613	0·00191	0·0344
D..............	0·01620	0·00190	0·0342
F..............	0·01619	0·00171	0·0294
Average for D.....	0·01605	0·00177	0·0314

for these differences calculated for 100°; this has been done for the sake of comparison only, and is not likely to be strictly correct, because the differences apparently are not the same for each degree of temperature. At any rate this is seen to be the case with the results obtained by Kettler with water, when they increase in magnitude as the temperature rises.

If an average of the differences obtained for the lines A, C, D, and F be taken, a number is obtained, which is practically that of D, and as it is thought that such an average is likely to give a more accurate number than that obtained for this line only, it has been taken whenever possible, and the D line has consequently been selected for comparison instead of the A line previously used.

The following atomic weights were used in the calculations:—

C = 12, H = 1, O = 16, N = 14, Cl = 35·5, Br = 80, I = 127.

Refractive Power of Water.

The results I have obtained with water are contained in the table on p. 292, and for the sake of comparison I also give those of Gladstone (*Phil. Trans.*, 1870, 28) and of Kettler (*Ann. Phys. Chem.*, **33**, 28); it will be remembered that the lithium line α is very nearly the same as C or H_α.

	Gladstone.	Kettler.	
	15°.	15°.	87·3°.
A	1·32924	—	—
α	—	1·33148	1·32035
D	1·33328	1·33365	1·32245

Kettler's numbers when calculated for $\frac{\mu - 1}{d}$ give for the difference of 68·7° (taken between 15° and 83·7°) for α and D 0·00136, which for 100° gives 0·00197 for α and 0·00198 for D. This is very close to the found numbers above, but a little higher than the average for D, and it is probable that this latter is a little low, as the differences found for A and F appear rather small when compared with C and D.

Heptane.

$d\frac{12·2°}{4°}$ 0·69026, $d\frac{88·8°}{4°}$ 0·62301.

Line.	μ.			$\frac{\mu - 1}{d}$.			$\frac{\mu - 1}{d}p$.		
	t.		Difference for 76·6°.	*t.*		Difference for 76·6°.	*t.*		Difference for 76·6°.
	12·2°.	88·8°.		12·2°.	88·8°.		12·2°.	88·8°.	
A..............	1·38754	1·34787	0·03967	0·56144	0·55837	0·00307	56·144	55·837	0·307
C..............	1·38966	1·34986	0·03980	0·56451	0·56157	0·00309	56·451	56·157	0·309
D..............	1·39178	1·35167	0·04011	0·56758	0·56446	0·00312	56·758	56·446	0·312
F..............	1·39664	1·35602	0·04062	0·57461	0·57145	0·00316	57·461	57·145	0·316
Average for D....	—	—	0·04005	—	—	0·00311	—	—	0·311

Difference for 100°.

A..............	0·05179	0·00401	0·401
C..............	0·05196	0·00403	0·403
D..............	0·05236	0·00407	0·407
F..............	0·05303	0·00412	0·412
Average for D.....	0·05228	0·00406	0·406

Gladstone's determinations gave (Trans , 1891, **59**, 292) at 12° μ_A 1·3875, μ_D 1·3917, μF 1·3966.

Octyl Iodide.

$d\frac{14{\cdot}5^\circ}{4^\circ}$ 1·34096, $d\frac{88{\cdot}5^\circ}{4^\circ}$ 1·25332.

Line.	μ.			$\frac{\mu-1}{d}$.			$\frac{\mu-1}{d}p$.		
	t.		Difference for 74°.	*t.*		Difference for 74°.	*t.*		Difference for 74°.
	14·5°.	88·5°.		14·5°.	88·5°.		14·5°.	88·5°.	
A..............	1·48448	1·45094	0·03354	0·36129	0·35979	0·00150	86·709	86·350	0·360
D..............	1·49166	1·45756	0·03409	0·36664	0·36508	0·00156	87·993	87·619	0·374
F..............	1·50024	1·46555	0·03470	0·37304	0·37144	0·00160	89·531	89·147	0·383

Difference for 100°.

A..............	0·04533	0·00203	0·486
D..............	0·04607	0·00211	0·506
F..............	0·04688	0·00216	0·518

Methylene Iodide.

$d\frac{8·4°}{4°}$ 3·3480, $d\frac{87°}{4°}$ 3·1390,

Line.	μ.			$\frac{\mu-1}{d}$.			$\frac{\mu-1}{d}p$.		
	t.		Difference for 78·6°.	*t.*		Difference for 78·6°.	*t.*		Difference for 78·6°.
	8·4°.	87°.		8·4°.	87°.		8·4°.	87°.	
A	1·72770	1·67538	0·05232	0·21735	0·21516	0·00219	58·249	57·662	0·587
C	1·73850	1·68533	0·05317	0·22057	0·21833	0·00224	59·114	58·512	0·602
D	1·74881	1·69462	0·05419	0·22365	0·22129	0·00236	59·939	59·305	0·634
F	1·77614	1·71994	0·05620	0·23182	0·22935	0·00247	62·127	61·467	0·660
Average for D	—	—	0·05397	—	—	0·00231	—	—	0·625

Difference for 100°.

A	0·06656	0·00279	0·747
C	0·06764	0·00286	0·766
D	0·06894	0·00300	0·807
F	0·07150	0·00313	0·840
Average for D	0·06866	0·00295	0·790

Toluene.

$d\frac{10\cdot7^\circ}{4^\circ}$ 0·87532, $d\frac{90\cdot35^\circ}{4^\circ}$ 0·79949,

Line.	μ.			$\frac{\mu-1}{d}$.			$\frac{\mu-1}{d}p$.		
	t.		Difference for 79·65.	t.		Difference for 79·65°.	t.		Difference for 79·65°.
	10·7°.	90·35°.		10·7°.	90·35°.		10·7°.	90·35°.	
A..............	1·49290	1·44784	0·04506	0·56311	0·56016	0·00295	51·806	51·535	0·271
C..............	1·49785	1·45231	0·04554	0·56876	0·56575	0·00301	52·326	52·049	0·277
D..............	1·50236	1·45639	0·04597	0·57391	0·57085	0·00306	52·800	52·518	0·282
F..............	1·51407	1·46694	0·04713	0·58729	0·58405	0·00324	54·031	53·733	0·298
Average for D....	—	—	0·04592	—	—	0·00306	—	—	0·282

Difference for 100°.

A..............	0·05657	0·00370	0·340
C..............	0·05717	0·00378	0·348
D..............	0·05771	0·00384	0·353
F..............	0·05917	0·00407	0·374
Average for D....	0·05765	0·00384	0·353

Phenyl Chloride.

$d\frac{9\cdot6}{4^\circ}$ 1·1167. $d\frac{89\cdot2^\circ}{4^\circ}$ 1·0302.

Line.	μ.			$\frac{\mu-1}{d}$.			$\frac{\mu-1}{d}p$.		
	t.		Difference for 79·6°.	*t.*		Difference for 79·6°.	*t.*		Difference for 79·6°.
	9·6°.	89·2°.		9·6°.	89·2°.		9·6°.	89·2°.	
A	1·51950	1·47762	0·04188	0·46519	0·46351	0·00168	52·334	52·156	0·178
C	1·52554	1·48252	0·04302	0·47057	0·46836	0·00221	52·942	52·691	0·251
D	1·53057	1·48698	0·04359	0·47510	0·47269	0·00241	53·449	53·178	0·271
F	1·54289	1·49843	0·04446	0·48613	0·48381	0·00233	54·690	54·429	0·261
G	1·55378	1·50826	0·04552	0·49588	0·49335	0·00254	55·787	55·502	0·285
Average for D	—	—	0·04324	—	—	0·00216	—	—	0·240

Difference for 100°.

A	0·05261	0·00211	0·223
C	0·05404	0·00278	0·315
D	0·05476	0·00302	0·340
F	0·05585	0·00292	0·328
G	0·05718	0·00318	0·358
Average for D	0·05431	0·00271	0·301

Phenyl Bromide.

$d\frac{4{\cdot}2^\circ}{4^\circ}$ 1·51000, $d\frac{89{\cdot}2^\circ}{4^\circ}$ 1·39638.

Line.	μ.			$\frac{\mu-1}{d}$.			$\frac{\mu-1}{d}p$.		
	t.		Difference for 85°.	*t.*		Difference for 85°.	*t.*		Difference for 85°.
	4·2°	89·2.		4·2°.	89·2.		4·2°.	89·2°.	
A	1·55663	1·51198	0·04465	0·36863	0·36665	0·00198	57·875	57·564	0·311
C	1·56252	1·51752	0·04500	0·37253	0·37062	0·00191	58·488	58·187	0·301
D	1·56796	1·52235	0·04561	0·37613	0·37408	0·00205	59·053	58·730	0·323
F	1·58201	1·53513	0·04688	0·38544	0·38323	0·00221	60·514	60·167	0·347
G	1·59439	1·54630	0·04809	0·39364	0·39123	0·00241	61·801	61·423	0·378
Average for D	—	—	0·04553	—	—	0·00204	—	—	0·320

Difference for 100°.

A	0·05253	0·00233	0·366
C	0·05294	0·00225	0·354
D	0·05366	0·00241	0·380
F	0·05515	0·00260	0·408
G	0·05658	0·00283	0·445
Average for D	0·05357	0·00239	0·377

Phenyl Iodide.

$d\frac{8^\circ}{4^\circ}$ 1·8482, $d\frac{88^\circ}{4^\circ}$ 1·72722.

Line.	μ.			$\frac{\mu-1}{d}$.			$\frac{\mu-1}{d}p$.		
	t.		Difference for 80°.	*t.*		Difference for 80°.	*t.*		Difference for 80°.
	8°.	88°.		8°.	88°.		8°.	88°.	
A	1·61263	1·56929	0·04334	0·33146	0·32959	0·00187	67·618	67·238	0·380
C	1·62003	1·57616	0·04387	0·33546	0·33358	0·00188	68·435	68·050	0·385
D	1·62707	1·58265	0·04442	0·33927	0·33733	0·00194	69·212	68·816	0·396
F	1·64524	1·59944	0·04580	0·34910	0·34705	0·00205	71·217	70·799	0·418
G	1·66126	1·61428	0·04698	0·35777	0·35565	0·00212	72·985	72·552	0·433
Average for D	—	—	0·04436	—	—	0 00191	—	—	0·395

Difference for 100°.

Line.	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
A	0·05417	0·00233	0·474
C	0·05484	0·00236	0·481
D	0·05552	0·00242	0·494
F	0·05725	0·00256	0·522
G	0·05872	0·00265	0·542
Average for D	0·05545	0·00242	0·494

Aniline.

$d\frac{11\cdot2^\circ}{4^\circ}$ 1·02792, $d\frac{90\cdot1^\circ}{4^\circ}$ 0·95783.

Line.	μ.			$\frac{\mu-1}{d}$.			$\frac{\mu-1}{d}p$.		
	t.		Difference for 78·9°.	*t.*		Difference for 78·9°.	*t.*		Difference for 78·9°.
	11·2°.	90·1°.		11·2°.	90·1°.		11·2°.	90·1°.	
A	1·57644	1·53530	0·04114	0·56078	0·55886	0·00192	52·153	51·974	0·179
C	1·58378	1·54202	0·04176	0·56792	0·56587	0·00205	52·816	52·626	0·190
D	1·59073	1·54833	0·04240	0·57469	0·57247	0·00222	53·446	53·239	0·207
F	1·60882	1·56515	0·04367	0·59228	0·59003	0·00225	55·082	54·873	0·209
G	1·62045	1·57594	0·04451	0·60359	0·60129	0·00230	56·134	55·920	0·214
Average for D	—	—	0·04231	—	—	0·00211	—	—	0·196

Difference for 100°.

Line.	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
A	0·05214	0·00243	0·226
C	0·05293	0·00258	0·241
D	0·05374	0·00281	0·261
F	0·05535	0·00285	0·265
G	0·05642	0·00292	0·272
Average for D	0·05354	0·00267	0·248

Dimethylaniline.

$d_{4^\circ}^{8^\circ}$ 0·96688, $d_{4^\circ}^{89·7^\circ}$ 0·89961.

Line.	μ.			$\frac{\mu-1}{d}$.			$\frac{\mu-1}{d}p$.		
	t.		Difference for 81·7°.	t.		Difference for 81·7°.	t.		Difference for 81·7°.
	8°.	89·7°.		8°.	89·7°.		8°.	89·7°.	
A	1·55106	1·51048	0·04058	0·56983	0·56745	0·00238	68·962	68·661	0·301
C	1·55828	1·51704	0·04124	0·57740	0·57474	0·00266	69·865	69·544	0·321
D	1·56489	1·52315	0·04174	0·58424	0·58154	0·00270	70·693	70·366	0·327
F	1·58369	1·53979	0·04390	0·60368	0·60003	0·00365	73·045	72·604	0·441
Average for D	—	—	0·04186	—	—	0·00285	—	—	0·347

Difference for 100°.

A	0·04966	0·00292	0·368
C	0·05047	0·00325	0·394
D	0·05108	0·00330	0·400
F	0·05373	0·00446	0·540
Average for D	0·05123	0·00348	0·425

α-Naphthylamine.

$d\frac{51^\circ}{4^\circ}$ 1·10043, $d\frac{88\cdot4^\circ}{4^\circ}$ 1·07207.

Line.	μ.			$\frac{\mu-1}{d}$.			$\frac{\mu-1}{d}p$.		
	t.		Difference for 37·4°.	*t.*		Difference for 37·4°.	*t.*		Difference for 37·4°.
	51°.	88·4°.		51°.	88·4°.		51°.	88·4°.	
A	1·64787	1·63015	0·01772	0·58874	0·58779	0·00095	84·190	84·054	0·136
C	1·65932	1·64109	0·01823	0·59914	0·59800	0·00114	85·673	85·513	0·165
D	1·67034	1·65176	0·01858	0·60917	0·60795	0·00122	87·111	86·936	0·175
F	1·70181	1·68211	0·01970	0·63776	0·63626	0·00150	91·200	90·985	2·215
Average for D	—	—	0·01856	—	—	0·00120	—	—	0·173

Difference for 100°.

Line.	μ.	$\frac{\mu-1}{d}$.	$\frac{\mu-1}{d}p$.
A	0·04737	0·00254	0·363
C	0·04872	0·00307	0·439
D	0·04962	0·00326	0·466
F	0·05268	0·00403	0·575
Average for D	0·04959	0·00322	0·461

Ethyl Cinnamate.

$d\frac{12{\cdot}9^\circ}{4^\circ}$ 1·05560, $d\frac{91{\cdot}1^\circ}{4^\circ}$ 0·98815.

Line.	μ.			$\frac{\mu-1}{d}$.			$\frac{\mu-1}{d}p$.		
	t.		Difference for 78·2.	*t.*		Difference for 78·2.	*t.*		Difference for 78·2.
	12·9.	91·1.		12·9.	91·1.		12·9.	91·1.	
A..............	1·54791	1·51081	0·03710	0·51905	0·51693	0·00212	91·353	90·980	0·373
C..............	1·55588	1·51797	0·03791	0·52660	0·52418	0·00242	92·682	92·256	0·426
D..............	1·56351	1·52500	0·03851	0·53383	0·53129	0·00254	93·954	93·508	0·446
F..............	1·58466	1·54422	0·04044	0·55387	0·55074	0·00313	97·480	96·931	0·549
Average for D....	—	—	0·03849	—	—	0·00255	—	—	0·449

Difference for 100°.

A..............	0·04744	0·00271	0·477
C..............	0·04847	0·00310	0·545
D..............	0·04924	0·00327	0·571
F..............	0·05171	0·00399	0·703
Average for D....	0·04921	0·00325	0·574

Thymol (Nasini and Bernheimer).

$d\frac{24·4°}{4°}$ 0·96895, $d\frac{77·3°}{4°}$ 0·92838.

Line.	μ.			$\frac{\mu - 1}{d}$.			$\frac{\mu - 1}{d}p$.		
	t.		Difference for 52·9°.	*t.*		Difference for 52·9°.	*t.*		Difference for 52·9°.
	24·4°.	77·3°.		24·4°.	77·3°.		24·4°.	77·3°.	
α	1·51453	1·49189	0·02264	0·53102	0·52984	0·00118	79·653	79·475	0·177
D.............	1·51893	1·49600	0·02293	0·53556	0·53426	0·00129	80 334	80·139	0·194
β	1·53012	1·50665	0·02347	0·54710	0·54573	0·00137	82·066	81·860	0·206

Difference for 100°.

α	0·04279	0·00223	0·335
D...	0·04334	0·00245	0 367
β	0·04136	0·00259	0·389

Cinnamic Alcohol (Nasini and Bernheimer).

$d\frac{24·8°}{4°}$ 1·04017, $d\frac{77·3°}{4°}$ 1·00027.

Line.	μ.			$\frac{\mu-1}{d}$.			$\frac{\mu-1}{d}p$.		
	t.		Difference for 52·5°.	*t.*		Difference for 52·5°.	*t.*		Difference for 52·5°.
	24·8°.	77·3°.		24·8°.	77·3°.		24·8°.	77·3°.	
α	1·57311	1·54939	0·02372	0·550977	0·549242	0·001735	73·8309	73·5984	0·2325
D	1·57990	1·55566	0·02424	0·557505	0·555510	0·001995	74·7057	74·4385	0·2672
β	1·59603	1·57301	0·02302	0·573012	0·572855	0·000157	76·7836	76·7626	0·0210

Difference for 100°.

α	0·04518	0·003304	0·4428
D	0·04617	0·003800	0·5089
β	0·04383	0·000299	0·0400

From the foregoing results, it will be seen that all the substances examined show a reduction of refractive power when heated, this reduction varying in amount for each substance. This is also found to be the case in examining the results obtained by Nasini and Bernheimer.

With respect to dispersion, the influence of heat appears to have a slight effect. If the difference of the molecular refraction between the lines which are wide apart be compared for the results obtained at low and high temperatures, it is seen that they are not the same, the difference being smaller for high temperature. Phenyl bromide and aniline may be taken as examples.

	Line.	*t*. 4·2 .	*t*. 89·2°.
Phenyl bromide	G	61·801	61·423
"	A	57·875	57·564
Difference between A and G......	....	3·926	3·859
		t. 11·2°.	*t*. 90·1°.
Aniline.......................	G	56·134	55·920
"	A	52·153	51·974
Difference between A and G......	....	3·981	3·946

In the first case, the dispersion appears as 0·067, and in the second 0·035, lower for high temperatures, but it is not so much as this, as the molecular refraction is represented by lower numbers at high than at low temperature, but if the ratio between the numbers for the low temperature be calculated for those of the higher temperatures, the real difference will be found; thus, in the case of phenyl bromide,

$$\text{As}\quad \overbrace{61{\cdot}801 : 57{\cdot}875}^{t.\ 4{\cdot}2^\circ.} \;::\; \overbrace{61{\cdot}423 : 57{\cdot}521}^{t.\ 89{\cdot}2^\circ.}.$$

The found number 57·564 giving a difference from the calculated of 0·043. This is for 85°, or about 0·050 for 100°. These amounts are very small, and might be passed over, only they are all in the same direction, and on examining the numbers given by Nasini and Bernheimer, the same thing is observed.

On calculating the results for the refraction of the substances examined above by Lorenz's formulæ, the results obtained for high temperatures give higher numbers than those for low temperatures. This is also shown to be the case from the tabulated results in the paper by Nasini and Bernheimer, indicating that these formulæ are not applicable for high temperatures.

The following table is arranged in the order of the refractive indices of the substances which have been examined, with the difference for the refractive energy and molecular refraction found for 100°, the D line being taken—

	t.	μ_D.	Difference for $\frac{\mu_D - 1}{d}$.	Difference for $\frac{\mu_D - 1}{d}p$.
Water.................	15·0°	1·33362	0·00190	0·031
Heptane...............	12·2	1·39178	0·00407	0·407
Octyl iodide...........	14·5	1·49166	0·00211	0·506
Toluene...............	10·7	1·50236	0 00384	0·353
Thymol................	24·4	1·51893	0·00245	0·367
Phenyl chloride.........	9·6	1·53057	0·00271	0·301
Ethyl cinnamate	12·9	1·56351	0·00325	0·574
Dimethylaniline.........	8·0	1·56489	0·00330	0·400
Phenyl bromide.........	4·2	1·56796	0·00241	0·380
Cinnamic alcohol........	24·8	1·57990	0·00380	0·509
Aniline................	11·2	1·59073	0·00267	0·248
Phenyl iodide...........	8·0	1·62707	0·00242	0·494
α-Naphthylamine	51·0	1·67034	0·00322	0·461
Methylene iodide........	8·4	1·74881	0·00300	0·807

From this we see that there is no relationship between these differences and the refractive indices. If, however, the substances of the aromatic series be taken alone and tabulated according to their refractive energy, cinnamic alcohol excepted, it is found that they group themselves, and the differences for 100° become more or less closely related.

	$\frac{\mu_D - 1}{d}$.	Difference for 100.	$\frac{\mu_D - 1}{d}p$.	Difference for 100°.
Phenyl iodide	0·33927	0 00242	69·212	0·494
,, bromide........	0·37613	0·00240	59·053	0·380
,, chloride........	0·47510	0·00271	53·449	0·340
Ethyl cinnamate	0·53383	0·00325	93·954	0·571
Cinnamic alcohol	0·55750	0·00380	74·706	0·509
Thymol...............	0·53556	0·00245	80·334	0·367
Toluene...............	0·57391	0·00384	52·800	0·353
Aniline	0·57469	0·00267	53·446	0·261
Dimethylaniline	0·58424	0·00348	70·693	0·400
α-Naphthylamine	0·60917	0·00322	87·111	0·466

Here it is seen that the differences do not vary with the refractive energy, but that each group of substances has differences of its own. In the case of the halogen compounds of phenyl, these only vary from 0·00240 to 0·00271; most likely, if the numbers were absolutely accurate, phenyl bromide would give a difference somewhere intermediate between the chloride and iodide. In the case of ethyl cinnamate and cinnamic alcohol, a very close accord cannot be expected, because, although they are both unsaturated compounds and related to each other, yet in composition they differ. The group of three bases comes last, and the variations here, considering the difference of their composition, are not very great.

Unfortunately, in the fatty series there have not been any closely-related substances examined so as to fall into groups, but the differences are quite as large as in the aromatic series.

Do these results in any way coincide with those obtained from the magnetic rotations? That the refractive and magnetic rotatory powers of substances are reduced by heat is certainly true, and for some time I was inclined to think the analogy ended there, but when the numbers are arranged as in the last table it would appear that it goes further.

In considering this, it is necessary to compare the differences obtained for the *molecular refraction* with those of the *molecular magnetic rotation.* Taking the halogen compounds of phenyl, it will be seen from the last table that the differences rise from the chloride to the bromide, and then to the iodide. In the magnetic rotation they behave in the same manner.

Ethyl Cinnamate and Cinnamic Alcohol.—Here again the same kind of analogy is seen, the differences going in the same direction, and in both cases are larger than those of saturated compounds nearly related to them. The bases aniline, dimethylaniline, and α-naphthylamine give results which also are of the same kind as the magnetic rotation, aniline giving the smaller, and α-naphthylamine the larger, difference.

Water is an exception. In the case of the magnetic rotation, no change has been found in its rotations for different temperatures, beyond that due to change of density; the difference in respect to its molecular refractive power is, however, very small.

The relations of these differences to the molecular refraction are not the same as those found in reference to the molecular magnetic rotations; for example, aniline gives a small, and phenyl iodide a rather large, difference in the former, but both have large ones in the latter case. Again, thymol and toluene have similar ones in the former, whilst toluene has a larger one than thymol in the latter case. In both instances, methylene iodide gives large results.

In the fatty series, the differences in the molecular magnetic rotations due to variations of temperature are always smaller than in the aromatic series, but in their molecular refraction they are apparently as large or larger; thus, with heptane and octyl iodide, they are larger than those of toluene and phenyliodide.

XXIV.—*Estimation of Oxygen Dissolved in Water.*

By Matthew A. Adams, F.R.C.S., F.I.C.

Although it is something like 15 years since Schützenberger published his process for the volumetric estimation of oxygen in water by means of hyposulphite of soda, that process, on the one hand, has never been superseded, nor, on the other, has it ever become established as a common everyday practical method for ordinary use, although many attempts have been made to render the original process more perfect and better adapted for the purposes of the technical chemist.

Passing over the earlier of these attempts by König and Mutschler, Tiemann and Preusse, Hutchinson, Bernthsen, and others, we find Dr. Dupré describing a modification of it in the pages of the *Analyst*, which I, in common, I believe, with many others, used with confidence till the publication of Roscoe and Lunt's contribution to this subject (Trans., 1889, **55**, 552).

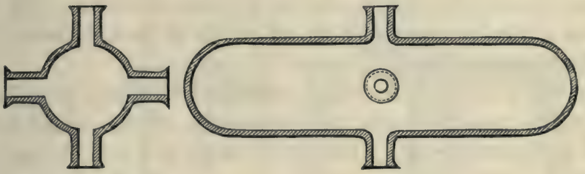
In that paper it is pointed out that the process, as previously employed, was open to grave error, owing to the diffusion of dissolved oxygen out of the water into the atmosphere of hydrogen in which the experiment was ordinarily conducted, also on account of diffusion of atmospheric oxygen from without into and through the long india-rubber tubes which form essential parts of the apparatus as employed by Dupré.

In the endeavour to avoid these risks, Roscoe and Lunt make the apparatus they employ so complicated and so unportable as in great measure to render their method unsuitable for technical use.

It was with a view of meeting these objections, in a manner simple and convenient, that I was led to design the apparatus now about to be described, which will, I hope, furnish the chemist with a means by which the volumetric estimation of oxygen in water may be accomplished with ease and absolute freedom from the ordinary sources of error that have been pointed out by Roscoe.

The *essential principle of my method* is that the water under examination, from first to last, shall be kept beyond the possibility of contact with any gaseous medium whatever, and the *essential feature of the apparatus* is that the whole process is conducted in a closed glass vessel, into which the water under examination, together with the necessary reagents, is admitted, but to the entire exclusion of any kind of atmosphere.

The apparatus consists, in the first place, of a specially constructed vessel, the *laboratory vessel*, made of stout glass of about 350 c.c. capacity, cylindrical in shape, 20 cm. long and 5 cm. in diameter, closed at both ends, and having four tubulures at its centre, set at equal distances around its circumference. This is mounted upon a wooden stand, two opposite tubulures resting upon the wooden support, like the trunnions of a cannon, so placed that it can be rocked in the vertical plane around its transverse axis. Attached to the wooden stand is a vertical prolongation with arms which carry two burettes, one intended for the indigo indicator, the other for the hyposulphite reagent, the one being connected to the left and the other to the right hand tubulures, each being controlled by a fixed pinch-cock. Attached to the bottom tubulure is a flexible tube communicating with a reservoir of mercury, and to the top tubulure is fitted the stem of a Y-tube, one branch serving as the inlet to the laboratory vessel from the supply of water under examination, and the other as outlet; this latter, discharging into a graduated cylinder, gives the means of measurement. Each of these tubes is also controlled by a pinch-cock.



Laboratory vessel. Quarter size. Transverse and Longitudinal Sections.

The hyposulphite burette is supplied from a stock bottle by siphon action, in the usual manner, and the hyposulphite solution, both in the burette and the stock bottle, is protected by a layer of light petroleum, besides which, as an additional protection against access of atmospheric oxygen, the spaces above the light petroleum in the burette and stock bottle are in free communication with a tube conveying common illuminating gas.

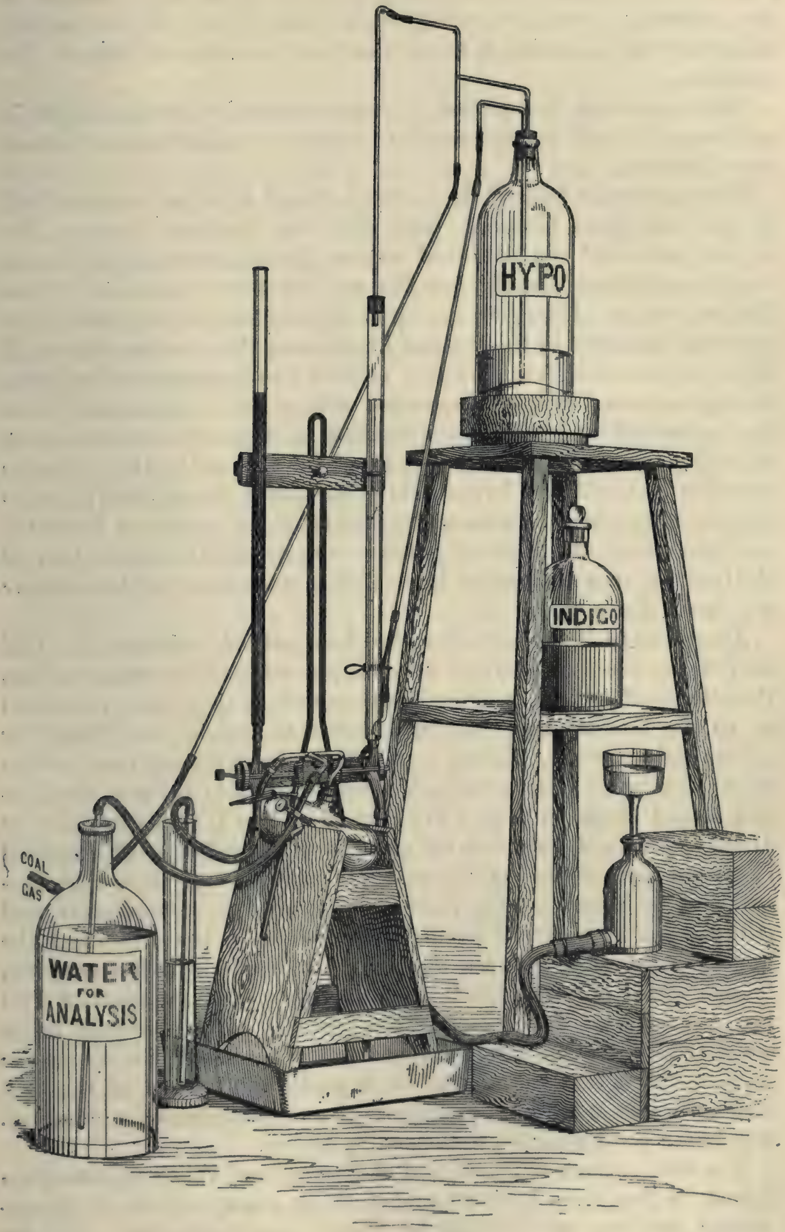
The mercury reservoir is of the ordinary kind, with tubulure near the bottom, and the mouth is closed with an india-rubber cork, perforated to receive the narrow stem of a funnel; on this stem a mark is made, for a purpose to be presently explained.

The mode of working requires but little explanation; the water to be examined and the reagents are aspirated into the laboratory vessel or expelled out of it by the effect of the gravity of mercury. To commence an experiment, the laboratory vessel is first completely filled with mercury by raising the reservoir; and then by lowering it, the water for analysis is gently aspirated into the laboratory vessel; when the retreating mercury rises to the mark on the stem of the funnel attached to the reservoir, the full charge of water required for the experiment has been taken into the laboratory vessel, and this being a fixed quantity, that can easily be repeated again and again with great exactitude, it constitutes a fundamental unit of measurement, the actual amount (which, in point of fact, is some 170 c.c.) being of no importance.

In this way water is introduced into the laboratory vessel until it is a little more than half full, the remainder of the space being still occupied by mercury; the level of the latter is a trifle below the apertures which give admission to the reagents. Each of these apertures is occupied by a glass tube passing through an india-rubber cork, and having an india-rubber valve, which, whilst allowing ingress of the reagent into the laboratory vessel, prevents either reflux or diffusion taking place into the burettes.

On introducing the indigo solution into the cylinder, the water becomes coloured, and under it we have the strongly reflecting surface of the mercury, so that when the hyposulphite is run in, and the vessel rocked upon its trunnions to effect a mixture of the reagents with the water, the minutest change of colour is at once made manifest, and the end of the reaction controlled with the utmost possible precision; I have mentioned that the water, when admitted, is taken in until the mercury rises to the mark on the stem of the funnel; this funnel allows space for the mercury displaced from the laboratory vessel on the admission of the reagents. At the conclusion of each experiment the mercury reservoir is raised, and the watery contents of the laboratory vessel discharged through the outlet branch of the Y-tube into the measuring cylinder, so that, if it is desired to ascertain the precise volume of water operated upon, this can easily be done by subtracting the amounts of the reagents used from the total bulk of the discharged fluid; this ended, the apparatus is again ready for the next experiment.

One, and certainly not the least, of the incidental advantages of this instrument is that the water operated upon can be taken into the laboratory vessel from any situation, high or low down beneath the


HYPO
INDIGO
COAL GAS
WATER FOR ANALYSIS

surface of the water, either as it exists in its natural position or in the collecting vessel, and, moreover, so quietly that it reaches the laboratory vessel, having suffered the least possible mechanical disturbance.

Before relating the results of experiments with my apparatus, it will be well to call to mind some of the recorded experiences of former experimenters.

Schützenberger himself first observed, and this has been verified by all who have followed him, that the reaction between the hyposulphite and the dissolved oxygen is not accomplished in an evenly-continuous manner, but the end reaction is reached by two distinct stages. Moreover, he found that by varying the method or order of procedure in the steps of his process, the relative position of those stages was altered; his *first* method was to commence by introducing the water into his apparatus, adding the indicator, and then the hyposulphite; by his *second* method, he began by introducing an indefinite amount of warm water, to which was added the indicator and then just sufficient hyposulphite to destroy the colour of the indicator, after which a measured quantity of the water to be tested was introduced, the effect of which was to restore the blue colour of the indigo; upon that more hyposulphite was added until the colour was again discharged.

According to Schützenberger, the first method estimates the half only of the dissolved oxygen actually present, and he suggests that the other half combines with the water to form hydrogen peroxide; as to the formation of hydrogen peroxide, König and Mutschler agree; subsequently, Ramsay and Williams in great measure confirm Schützenberger's observations, but make the ratio between the first and second stages to be as 3 to 5 instead of 1 to 1, and, moreover, by direct experiment, they test the question of the influence of dissolved hydrogen peroxide on the hyposulphite reagent, and show that peroxide of hydrogen is only *partially* estimated by hyposulphite, and that the partition of the oxygen between the indigo-white and the hyposulphite varies with the degree of dilution and the temperature; in one series of experiments 20·2 per cent. and in another 17·3 per cent. only of the oxygen of the peroxide actually present being estimated by reaction with the hyposulphite, the conclusion they come to, however, is that if the reaction is pushed to the end of the final stage, the two methods of procedure give results which are identical. The latter point was also confirmed by Dupré.

The observations of Dupré and of Ramsay and Williams were published in the years 1885–86, and I think I may say the Schützenberger process, as modified by Dupré, was extensively used for technical purposes; speaking for myself, I used it with every confidence until the middle of 1889, when, in conversation with Sir H. Roscoe, I found that discredit was cast upon an important series of observations I had made concerning the pollution of the River Medway, on the ground that the Schützenberger process as hitherto employed involved sources of error equal to 47 per cent. in proportion to the length of time occupied in the execution of the titration with the hyposulphite, and in the Transactions for 1889 is a paper by Roscoe and Lunt setting forth the grounds upon which this belief had been based; according to their observations, the following facts, among others, were established:—

1. That water holding oxygen in solution and contained in a vessel along with pure hydrogen gives up a part, and, in course of time, practically the whole, of its dissolved oxygen by diffusion into the supernatant hydrogen.

2. That the size and shape of the vessel in which the experiment is conducted, in so far as it exposes a larger surface of the water and contains a greater bulk of the hydrogen atmosphere, effects this diffusion with proportionate rapidity.

3. As a "positive proof that when pure hydrogen comes into contact with aërated water it is contaminated with oxygen, they record an experiment to show that when hydrogen so contaminated is imprisoned above a solution which will indicate the presence of oxygen by the formation of a blue colour, this blue colour is first observed at the surface of the liquid."

Acting upon these convictions, the method of Roscoe and Lunt is so contrived that the water operated upon is kept as far as possible out of contact with the hydrogen, the essential feature of the manipulation being that Schützenberger's process is inverted, that is, instead of the reducing agent being added to the water, the aërated water is introduced into, and beneath the surface of, the reducing agent, so that the free oxygen of the water may at once combine with the hyposulphite before it has a chance of diffusing into the hydrogen.

These observers take no other account of the two distinct stages in the titration, as recorded by previous experimenters, than appears to be implied in a proposition that the second stage is due to the reabsorption into the liquid of the oxygen diffused into the hydrogen atmosphere; neither do we find any allusion to the suggested formation of peroxide of hydrogen in the course of the reaction.

The scheme of my apparatus being very simple, and its application so obvious, a detailed description of the practical working with it is hardly required, the principle involved being precisely the same as that concerned in other processes; consequently a cursory description is all that is necessary, and even this more for the sake of the opportunity it affords for recording certain interesting points, one of which at least must have an important fundamental bearing upon any process in which Schützenberger's reagent is employed.

In actual practice at the outset we ascertain :—

1. The oxygen value of the indicator in terms of hyposulphite reagent.

2. Next, we carefully standardise the hyposulphite reagent by fully aërated distilled water, noting temperature and barometric pressure and using Roscoe's table.

3. We are then in a position to estimate the oxygen dissolved in the sample under examination.

1. With respect to the *indicator*, for reasons which will presently appear, I have made a large number of experiments to ascertain whether indigo-carmine, the agent usually employed, is the best for the purpose, and whether this substance could by any possibility play any other part than the passive one, of an indicator pure and simple; these experiments have included trials with Bismarck-brown, nigrosin, methyl-blue, &c., but I much prefer indigo-carmine. The first two are not properly reduced by the hyposulphite; methyl-blue is, but as it becomes perfectly colourless, it does not afford so sharp an end reaction as the golden-yellow of the indigo-carmine in its reduced condition; this yellow tint, being complementary to the blue of the oxidised state, forms a most striking contrast and affords the best possible indication of the end reaction. As regards the amount of the indicator to be employed, it is desirable that the coloration should not be too dense: 5 c.c. of a solution containing 0 5 gram of indigo-carmine to a litre of water constitutes a suitable strength, the blue colour of which, on the instant of the end point being reached, flashes into a golden-yellow, and lighted up by the brilliant reflection from the surface of the mercury, marks the end of the reaction in the most satisfactory manner.

We determine its hyposulphite value by running into the laboratory vessel about 100 c.c. of water, and adding a few drops of the indigo; the colour thereby produced is then exactly discharged by hyposulphite; then 15 c.c. of indigo are run in and the amount of hyposulphite now required to discharge the colour exactly noted; this is repeated with another 15 c.c. of indigo, and the total hyposulphite used in the two experiments divided by 6 gives the allowance to be made for the hyposulphite used up by the 5 c.c. of indicator employed in each experiment. To make sure that the amount of indicator employed has no perturbing influence, a number of experiments were made, and as the following series show, it is without effect.

Aërated Tap Water.

Number of experiments.	Amount of indigo solution used, each 5 c.c. of which consumed 1·38 c.c. of hyposulphite.	Hyposulphite actually consumed by the water corrected to constant volume.	Limit of experimental error.
6	5 c.c.	12·41	−0·03
3	10 „	12·34	−0·12
2	15 „	12·52	+0·06
2	20 „	12·58	+0·12
13		Mean 12·46	=0·12

2. With respect to the *hyposulphite reagent*, it is very important that in its preparation only as small an excess of lime as possible should be used, this reagent, when strongly alkaline, being far less sensitive, so that the sharpness of the end point is much impaired. It is well, also, to recall to mind that this reagent is very unstable and must be standardised at least once a day, and as it appears to me this instability is promoted by exposure to light, I am in the habit of keeping the stock well protected so as to entirely exclude light; having regard to the size of our laboratory vessel, it is desirable that the hyposulphite should be of such a strength that about 10 to 12 c.c. suffice for a single experiment.

3. As respects the actual operation of the experiment, in the first place it is to be remarked that where by Roscoe's method it is possible to conduct the experiment in the invert manner only, that is to say, by adding the aërated water to be tested to the reducing agent, with my apparatus we can pursue either the indirect method of Roscoe or the direct method of Schützenberger, a circumstance which has revealed points of interest now to be recorded.

As a first result of our new method, it was confidently expected that all distinction of first and second stages would have been abolished, but, to our surprise, upon trial we found that these two stages were as strongly manifest as ever; for example:—

Sample aërated tap water.	To end of first stage.	Difference.	Total to end of second stage.
Direct titration consumed of hyposulphite	15·66	6·12	21·78
Indirect do. do. do.	17·23	4·37	21·60

Moreover, we still encountered the same difficulty as our predecessors, for it seemed impossible to discover any fixed ratio between the first and second stages. At this point of our research we were as much, indeed even more, in the dark than ever, for our experiments appeared to upset Roscoe's deductions altogether, without any compensatory advance on our part; it was at this stage that we made a thorough investigation of the bearing of the indicator, and failing any explanation from this quarter, we turned our attention to the mercury, which was an ordinary commercial sample of reasonable purity; this was now purified, by thoroughly washing it by agitation with a solution of mercurous nitrate, and filtering; on replacing it in the apparatus, much to our satisfaction, the first stage altogether vanished, the end reaction came out sharp and clear without the shadow of anything to indicate a return of the blue, and it seemed the object desired had been attained; not so, however, for when we came to look into the matter more critically, we were met by another surprise. Remember our process admits of the direct as well as the indirect method of procedure; when these two modes came to be compared, it was found that the results did not agree, the indirect method always consumed *more* hyposulphite than the direct method, and it soon became evident that the results obtained by the direct method could be made to vary among themselves very largely, according to the speed with which the experiment was conducted, and this, notwithstanding there was no second stage and no atmosphere or impurity in the mercury to which diffusion or detention of the lost oxygen could be attributed. This could not be accounted for, therefore, on the supposition that the cause of it was the source of error pointed out by Roscoe. On this account we came to the conclusion that it is necessary to conduct the experiment in the indirect manner by adding the water under examination to the hyposulphite reagent, first of all, however, as a matter of expedience, having ascertained by a direct experiment the amount of hyposulphite reagent likely to be required for the indirect method.

The following examples illustrate this:—

Average of	4	experiments,	quick, direct used,	15·12	hyposulphite.
,,	3	,,	slow ,, ,,	13·60	,,
,,	3	,,	reversed, indirect used	15·81	,,

From this it would appear that although our experiments are not in direct conflict with the diffusion theory of Roscoe and Lunt, they at least show that their reasoning is insufficient to account for the facts of the case, and that there is something else to be considered besides the liability of diffusion of the dissolved oxygen into the supernatant atmosphere contained in the vessel in which the experiment is conducted.

These *two mysteries* revealed by my experiments have been made the subject of numerous experiments with the object of discovering a satisfactory explanation. Speaking with reserve, I am inclined to attribute the first of these to the presence of mercurous oxide, and the second to the formation of hydrogen peroxide; our reason for the first of these opinions is as follows:—We had noticed that the surface of the impure mercury, before it had been washed with mercurous nitrate, had a more or less dirty scum on its surface, which was, of course, entirely removed by filtration before the mercury was returned to the laboratory vessel. I believe that this was mercurous oxide, and that it was temporarily converted by nascent oxygen into mercuric oxide, but afterwards returned to the mercurous state as it slowly gave up its extra atom of oxygen under the more powerful affinity of the surplus hyposulphite consumed by the indigo, thereby restoring the indigo to its blue colour.

With regard to the formation of hydrogen peroxide, all our endeavours to obtain direct evidence of the presence of this substance have as yet failed; careful experiments have been made with chromic acid and ether, and also with titanic acid solution, but always, so far, with a negative result. Notwithstanding this, however, I am strongly inclined to believe that under certain circumstances hydrogen peroxide is formed, and that we shall yet be able to prove it.

Be this as it may, beyond all doubt, in the estimation of the oxygen dissolved in water by the Schützenberger process, the result obtained is liable to differ in accordance with the speed with which the experiment is performed, it being always higher with a quick and lower with a slow titration.

It follows either that too much is recorded by the quick titration, or too little by the slow.

The question therefore is, what is the explanation of these differences, and which of the two modes of working affords the correct estimate?

As it appears to me, the *factors* and *conditions* concerned are as follows:—

1. Water containing oxygen dissolved.
2. An indigo indicator, blue in its oxidised, and yellow in its reduced condition.
3. A reducing agent, the hyposulphite of sodium.
4. It may be confidently assumed that the oxygen dissolved in the water exists in the molecular state.
5. And that the first effect of the introduction of the hyposulphite

molecule is to break up the bond of the oxygen molecule, thereby causing atomic or nascent oxygen to be set at liberty.

6. Moreover we may with a fair amount of confidence also assume that when a molecule of hyposulphite attacks a molecule of oxygen destroying the molecular bond of the latter, there must as a consequence be one of the atoms of oxygen nascent, whilst the other is fixed by the hyposulphite molecule. What more likely than that this free nascent oxygen atom should attach itself to a molecule of water, and produce a corresponding molecule of hydrogen peroxide, and if so, there is an end to our difficulty; the explanation is simple enough, for when the hyposulphite is introduced *quickly*, the freed oxygen atoms are delivered into the presence of an abundance of hyposulphite molecules ready to fix the liberated oxygen atoms forthwith; but on the other hand, when the hyposulphite is introduced *slowly*, free oxygen atoms finding themselves in the presence of oxidised hyposulphite are compelled to seek fresh bonds of attachment, and before molecular oxygen can be wholly re-formed, to some extent, at all events, hydrogen peroxide is produced; now, as it has been shown by Ramsay and Williams that hydrogen peroxide is only partially reduced by the hyposulphite, it follows that by slow titration the conditions of our experiment are so far charged that we have *a priori* reason to expect that a portion of the oxygen originally dissolved in the water will escape from fixation by the hyposulphite, and so account for the lower estimate which the slow titration affords.

In conclusion, I wish to acknowledge, most cordially, the painstaking and skilful help rendered to me in the progress of this research by my friend and assistant Mr. Lionel Stansell.

Addendum.

For the convenience of those who desire to adopt this method, I may mention that all the constituent parts of the apparatus, with exception of the "laboratory vessel," may usually be found amongst the usual furniture of any laboratory.

"Laboratory vessels" have been made for me by Messrs. Powell, of the Whitefriars Glass Works, and also by Greiner, of Munich (Neuhauserstrasse, 49).

As to the valve at the extremity of each burette within the laboratory vessel to which allusion has been made, it may be constructed in the following simple manner:—A piece of narrow india-rubber tube about 15 mm. long, has a slit 5 mm. long, longitudinally placed at the centre of its upper aspect, made by a single clean cut with a chisel; one end of this india-rubber tube is slipped over the end of the burette, and the other free end is stopped with a fragment of glass rod; the intervening slit in the india-rubber tube acts admirably as the valve in question.

It is always desirable in collecting a sample for examination, that the least possible mechanical disturbance of the water should take place during the collection, and, further, it is often desired to obtain this sample from a stratum at some distance beneath the surface, for which purpose the following device will be found very convenient:—An ordinary Winchester pint bottle of tolerably thick glass is perforated on its side near the bottom, by a hole of 2 or 3 millimetres in diameter, this may be easily accomplished by means of a hard drill wetted with turpentine; into this is fitted a peg of soft wood like the vent peg of a beer cask, and the neck of the bottle is furnished with an india-rubber tube of any length desired. In use the bottle is inverted, the hole closed by the thumb, the india-rubber tube dropped into the water, and when its extremity reaches the desired depth, on withdrawing the thumb the water quietly enters the bottle. When full the peg is inserted, and the bottle withdrawn and stoppered with a short piece of india-rubber tube, the free end of which is closed by a piece of glass rod; this allows of expansion and contraction caused by change of temperature without entrance of atmospheric air or loss of dissolved oxygen *ex vacuo*.

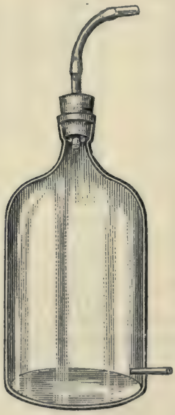


Table showing amounts of Dissolved Oxygen in Water when saturated. The various authorities are given. Cubic centimetres per litre N.T.P.

Degrees centigrade.	Bunsen.	Roscoe and Lunt, dry.	Winkler, dry.	Roscoe and Lunt, moist.	Pettersson and Sonden. ?	Dittmar, dry.
0	—	—	10·19	—	10·01	—
1	—	—	9·91	—	9·72	—
2	—	—	9·64	—	9·43	—
3	—	—	9·39	—	9·14	—
4	—	—	9·14	—	8·85	—
5	7·58	8·76	8·91	8·68	8·56	—
6	7·42	8·58	8·68	8·49	8·28	—
7	7·26	8·40	8·47	8·31	8·16	—
8	7·11	8·22	8·26	8·13	8·04	—
9	6·95	8·05	8·06	7·95	7·92	—
10	6·79	7·87	7·87	7·77	7·75	8·00
11	6·68	7·71	7·69	7·60	7·58	7·84
12	6·57	7·56	7·52	7·44	7·41	7·68
13	6·46	7·40	7·35	7·28	7·25	7·52
14	6·35	7·25	7·19	7·12	7·02	7·36
15	6·25	7·09	7·04	6·96	—	7·20
16	6·18	6·96	6·89	6·82	—	7·06
17	6·12	6·83	6·75	6·68	—	6·93
18	6·05	6·70	6·61	6·54	—	6·80
19	5·99	6·57	6·48	6·40	—	6·66
20	5·93	6·44	6·55	6·28	—	6·53
21	—	6·33	6·23	6·16	—	6·41
22	—	6·23	6·11	6·04	—	6·30
23	—	6·12	6·00	5·94	—	6·19
24	—	6·02	5·88	5·84	—	6·08
25	—	5·91	5·77	5·76	—	5·97

XXV.—*The Luminosity of Coal-Gas Flames.*

By VIVIAN B. LEWES, Royal Naval College, Greenwich.

IN the autumn of 1890, I gave a course of Cantor lectures on gaseous illuminants, and in connection with these made a considerable number of experiments on the causes of luminosity in flames. Since then I have, from time to time, worked at the subject, and in view of the interest created by Professor Smithells' paper, read before this Society in December, I venture to bring my results before you.

I do not propose to enter into the vexed question of how far carbon particles are essential for luminosity, or under what conditions flames containing dense vapours may become luminous, but will restrict myself to the causes of luminosity in the flame of ordinary coal gas and similar mixtures of gaseous hydrocarbons with combustible diluents.

The researches of Heumann, Soret, Burch, and the recent observations by Professor Stokes, place beyond question the presence of solid particles in a luminous gas, oil, or candle flame, and the only point on which any doubt still lingers is the kind of decomposition which leads to the liberation of the solid carbon particles.

Many attempts have been made to trace the chemical changes taking place within a flame, by withdrawing the flame gases during combustion, and determining their composition, and analyses made by Landolt (*Ann. Phys. Chem.*, 1856, **99**, 389—417) give a great deal of information about the actions taking place.

I have also made analyses of flame gases in order to trace the variations in quantity of the hydrogen, hydrocarbons, and carbon monoxide present in the centre of the flame at various heights, with the following results:—

		Hydrocarbons.		
	Hydrogen.	Unsaturated.	Saturated.	Carbon monoxide.
Gas in tube	57·08	4·38	33·99	2·63
½ inch above burner. .	52·90	4·00	32·00	3·00
1½ inch above burner.	12·30	1·53	10·20	3·26
Tip of inner cone....	2·35	1·98	7·80	6·52
Centre of outer cone .	0·13	0·45	0·50	1·51
Escaping unburnt from tip of flame..	nil	nil	0·39	1·18

These figures, as well as those obtained by Landolt, point to the fact that the hydrogen in the gas burns first, and that the saturated hydrocarbons also undergo a rapid diminution in quantity, whilst the unsaturated hydrocarbons only diminish very slowly until the top of the inner non-luminous zone has been reached, after which they quickly disappear in the luminous portion of the flame.

Carbon monoxide, however, increases largely in quantity up to the top of the inner cone, and then rapidly burns away in the luminous zone. This increase of the carbon monoxide during the first part of the combustion has been shown to take place in the Bunsen flame by Dr. Blochmann (*Annalen*, **168**, 295), and has also been observed by Professor Smithells under the conditions existing in his beautiful experiment of burning a flame in two parts.

The fact that the unsaturated hydrocarbons only slowly decrease in the inner zone, and then rapidly disappear in the luminous part of the flame, has naturally suggested the idea that it is to these compounds that the flame owes its luminosity; but, as far as I know, no one has attempted to ascertain whether the unsaturated hydrocarbons present at the top of the inner non-luminous zone are of the same character as those found in the coal-gas.

The undoubted presence of acetylene in the products escaping from a cooled flame, and the fact that the incomplete combustion of hydrocarbon gases always gives rise to the formation of this compound, suggested the idea that it might play an important part in the changes taking place in the interior of a flame, and experiments were made to ascertain if any appreciable quantity was formed by the destruction of hydrocarbons in the flame gases.

The coal gas used was that supplied by the South Metropolitan Gas Company, and analyses give as its composition:—

Hydrogen	57·08
*Unsaturated hydrocarbons	4·38
Saturated hydrocarbons	33·99
Carbon monoxide	2·63
Carbon dioxide	0·79
Nitrogen	0·96
Oxygen......................	0·15
Bisulphide of carbon	0·02
	100·00

* Containing acetylene, 0·035.

And this gas, when burnt in a standard London Argand at the rate of 5 cubic feet per hour, is of an illuminating value which averages 16·3 candle power.

The gas was burned at the end of an open tube and the flame gases were aspirated from the centre of the flame by means of a small platinum tube, 2 mm. in diameter, and were led into a glass bulb-tube, in which the sample for analysis of the total hydrocarbons was collected, and then through two Volhard's absorbing bottles, containing 20 c.c. of concentrated ammoniacal silver nitrate solution. This absorbs the acetylene with formation and precipitation of silver acetylide and silver, owing to the reducing action of the carbon monoxide, two absorbing vessels being quite sufficient to prevent any traces of the gas escaping absorption. The contents of the two bottles were filtered, the precipitate of silver acetylide carefully washed with water, and then treated on the filter very cautiously with dilute hydrochloric acid, until all action ceases. Acetylene is given off, and the precipitate then consists of a mixture of silver chloride and metallic silver. This, after washing, is digested with dilute ammonia, and the ammoniacal solution, after filtration, is then treated with nitric acid to precipitate the chloride, which is weighed in the usual manner, 1 gram of silver chloride corresponding to 0·09 gram or 87·03 c.c. of acetylene (Winkler).

Acetylene formed during the Incomplete Combustion taking place in the Interior of a Luminous Flame.

	Total unsaturated hydrocarbons.	Acetylene.
Gas in burner	4·38 per cent.	0·035 per cent.
½ an inch above rim of burner	4·00 ,,	0·340 ,,
1½ inches above rim of burner	1·53 ,,	0·560 ,,
Tip of inner cone	1·98 ,,	1·410 ,,
Centre of luminous zone.....	0·45 ,,	0·045 ,,
Tip of luminous zone........	nil	nil

Showing that in the interior of the luminous flame the hydrocarbons at once begin to undergo decomposition, giving rise to acetylene, which, by the time the top of the inner non-luminous zone is reached, constitute over 70 per cent. of the unsaturated hydrocarbons present. A small proportion of the other hydrocarbons, however, remains undecomposed, and penetrates into the luminous zone, where it and the acetylene are both decomposed by the higher temperature attained, a carbon is liberated, and this, being for a moment heated to incandescence, gives luminosity to the flame.

An ordinary flat flame was now experimented with, the gases being withdrawn and analysed in the same way as before.

Acetylene formed in the Inner Zone of a Flat Flame from a No. 7 Bray Burner.

Portion of flame.	Total unsaturated hydrocarbon.	Acetylene.	Other unsaturated hydrocarbons.
	Per cent.	Per cent.	Per cent.
¼ an inch from top of burner...	3·565	0·115	3·450
1¼ inches from burner.........	2·063	1·303	0·760
1¾ ,, ,, ...	1·393	1·133	0·260
2¼ ,, ,, ...	trace	trace	—

Showing that by the time the top of the non-luminous portion of the flame was reached over 81 per cent. of the hydrocarbons present had been converted into acetylene.

The next step was to determine the thermal conditions existing in the flat flame in order to see if they would give any definite information as to the actions taking place.

The beautiful platinum and platinum-rhodium thermo-couple devised by Le Chatelier, and introduced to us by Professor Roberts-Austen, gives a means of measuring the temperatures of flames with ease and comparative accuracy.

I made a small thermo-couple of platinum and 10 per cent. rhodium platinum wire, using it as thin as possible to reduce errors from loss of heat by conduction, and keeping the wires of considerable length to prevent any rise of temperature introducing conflicting currents at the connections with the galvanometer wires; a reflecting galvanometer of low resistance was employed, and sufficient resistance introduced into the circuit to keep the spot of light upon the scale at the highest temperature attained in the flame, and the scale was then graduated for temperature by taking water at 0° and 100°, and checking the higher temperatures by the fusing points of the chlorides of the alkalis and alkaline earths, as determined by Carnelley (*J. Chem. Soc.*, 1876, i, 489).

On mapping out the temperatures existing in a flat flame from a Bray burner consuming 7 cubic feet of gas per hour, it was found that in the inner non-luminous portion the temperature steadily increased from 500°, half an inch from the burner, to 1267° at the commencement of luminosity at the apex, whilst the centre had a temperature of 1014°, rising to 1216° at the luminous edges. In the centre of the luminous portion of the flame the temperature was 1166°, whilst the highest temperature was reached at the top of the flame, which gave 1368°.

These results, I think, help to explain the action taking place in the flame. In the inner non-luminous zone, the hydrocarbons heated up by the combustion of the hydrogen and some of the methane, undergo certain changes, which result in their conversion into acetylene, and this, being an endothermic compound, readily decomposible by heat or detonation into carbon and hydrogen, breaks up when a sufficient temperature is attained; owing, however, to the diluting action of the nitrogen and other flame gases, this does not take place until the top of the non-luminous zone is reached, where, at a temperature of a little over 1000°, the decomposition occurs with an increase of temperature, and the liberated carbon, being heated to incandescence, gives the luminosity to the flame.

Other luminous hydrocarbon flames were then tried, and the percentage of acetylene formed in the inner zone determined.

	Oil gas of 30 candle power.	Paraffin lamp.	Candle.
Acetylene	3·09 per cent.	2·222 per cent.	2·163 per cent.

I have made attempts to trace the actions which give rise to the acetylene, and to see if the carbon monoxide, which increases so rapidly in quantity in the inner flame, is due to the same actions, or is formed in some other way.

If it be heat alone which converts the hydrocarbons present into acetylene, then this result should be obtained by passing them alone, or diluted with hydrogen, through a very narrow tube, heated to the same temperature as that existing near the top of the dark zone of a luminous flame, that is, to a little way over 1000°.

The difficulty at once arises of obtaining a tube sufficiently narrow in bore to ensure the gas being heated to nearly the same temperature as the walls of the tube without using platinum, as all attempts to obtain a nickel or iron tube of the desired dimensions failed, and the use of platinum is open to the objection of the actions induced by its surface at the temperature employed.

In order to see if surface action would in any way affect the amount of acetylene formed, a very fine platinum tube and a pipe-stem glazed with borax were heated in the same furnace to the same temperature, and an equal amount of ethylene was passed slowly through both, and the acetylene formed estimated.

Acetylene formed with platinum tube = 0·494 per cent.
Acetylene formed with glazed pipe-stem = 0·432 per cent.

On now heating the pipe-stem to a higher temperature, the acetylene formed from the same amount of gas was 0·808, so that the smaller amount obtained in the previous experiment with the pipe-stem was evidently due to the thick, clay walls.

From this it appeared as if the platinum exercised no influence on the production of acetylene in the experiment, but as I also wanted to determine the action of small quantities of air upon the hydrocarbons, under the influence of the temperature existing in the inner zone of a flame, I made a second experiment, in which methane, free from unsaturated hydrocarbons, was passed with 10 per cent. of air through a pipe-stem, and through the platinum tube, both being heated to the same temperature, which was a little under 1000°:—

Gases after Heating.

	Pipe-stem.	Platinum tube.
Unsaturated hydrocarbons	1·92	1·52
Carbon monoxide.............	2·30	2·10
Carbon dioxide	1·01	0·51
Oxygen......................	0·54	0·51
Acetylene	trace	trace

With the pipe-stem it was almost impossible to get an even temperature much above that used in this experiment, but on passing the same mixture of methane and 10 per cent. of air through the platinum tube heated to about 1100—1200°, acetylene appeared in quantity:—

Unsaturated hydrocarbons	3·10
Acetylene	2·07

These experiments pointed to the platinum tube having so little action on the gases as to render its use admissible in the following experiments, and the difficulties arising from the pipe-stems not being straight, from the thick walls rendering it nearly impossible to attain even heating, and from constant fracture, were so great that I decided to use a platinum tube 2 mm. in diameter and a foot long for the following experiments:—

Methane was prepared by the action of the copper-zinc couple upon a mixture of methyl iodide and methyl alcohol, with the usual precautions, and was then passed through the tube, 6 inches of which were heated to 1000° in the flat flame of a broad Bunsen.

The methane employed contained 99 per cent. of saturated hydrocarbons, and was analysed for other constituents before and after heating:—

	Before heating.	After heating.
Unsaturated hydrocarbons	0·5	3·2
Acetylene	0·000	1·798
Carbon dioxide	0·00	0·00
Carbon monoxide	0·0	0·0

The effect of heating the methane with other gases present in the inner zone of the flame was then tried.

	Methane heated with			
	3 p. c. oxygen.	15 p. c. air.	50 p. c. carbon monoxide.	60 p. c. hydrogen.
Unsaturated hydrocarbons	2·0	2·0	1·0	1·47
Acetylene	1·426	0·656	0·887	0·473
Carbon monoxide	1·1	1·0	—	0·490

These experiments seem to point to acetylene being formed by the action of heat alone upon the methane, whilst as soon as oxygen is present carbon monoxide is also produced.

The experiment with oxygen and air also shows the retarding effect of dilution upon the formation of the acetylene.

The presence of carbon monoxide in the methane diluted with hydrogen was probably caused by the latter gas containing nearly

2 per cent. of oxygen, whilst I think the experiment with carbon monoxide shows that interactions between it and methane cannot give rise to acetylene, as the amount formed is just one-half that produced on heating methane alone, the reduction in quantity being due to dilution.

The action taking place is most probably a splitting up of the methane into acetylene and hydrogen—

$$2CH_4 = C_2H_2 + 3H_2,$$

and some of the acetylene is then polymerised into benzene, as noticed by Berthelot (*Compt. rend.*, **54**, 515).

The methane takes a far higher temperature for the formation of acetylene than any of the other hydrocarbons experimented with.

Ethane was prepared from ethyl iodide by the action of the copper-zinc couple, and contained 93 per cent. of saturated and no unsaturated hydrocarbons or acetylene; it, however, contained a trace of air, which would render estimation of carbon monoxide, after heating, useless.

	Heated alone.
Unsaturated hydrocarbons	19·47
Containing acetylene	8·224

Ethane Diluted with 80 *per cent. Hydrogen.*

		Heated with		
	Gas used.	15 p. c. air.	20 p. c. air.	25 p. c. air.
Unsaturated hydrocarbons	0·00	7·69	5·58	5·05
Acetylene	0·00	3·89	3·20	3·11
Carbon dioxide..........	0·00	0·00	1·01	1·51
Carbon monoxide........	0·00	1·54	2·53	3·03

Showing that the carbon monoxide is being formed in increasing quantities with the increase in the percentage of air, and that the amount of unsaturated hydrocarbons, other than the acetylene, are reduced in quantity more quickly than the acetylene itself; this, however, being probably due to their splitting up with formation of acetylene, and both slowly being oxidised.

These experiments show that when between 15 and 20 per cent. of air is present, carbon dioxide, as well as monoxide, begins to form.

Ethylene.—The gas was prepared by the action of sulphuric acid upon alcohol, and contained 93 per cent. unsaturated hydrocarbons, and neither carbon monoxide nor acetylene.

	Gas heated	
	Alone.	With 3 per cent oxygen.
Acetylene	8·894	7·165
Carbon monoxide....	0·000	5·74

Ethylene diluted with Hydrogen.

		Heated with	
	Gas used.	20 p. c. air.	25 p. c. air.
Unsaturated hydrocarbons ...	14·50	6·81	3·66
Acetylene..................	0·00	2·03	1·59
Carbon monoxide	0·00	5·30	3·73

These experiments, I think, show that dilution has a distinct effect in preventing the "over-cracking" of the hydrocarbons, as the proportion of acetylene to unsaturated hydrocarbons is far higher in the gas diluted with hydrogen than in the rich gas.

In another experiment, hydrogen was charged with 1·02 per cent. of benzene vapour, and heated with varying proportions of air, with the following results :—

	8 p. c. air.	13 p. c. air.	18 p. c. air.
Acetylene formed...........	0·026	0·032	0·218

It has been suggested that if acetylene is formed simply by the action of heat, it ought to be present in quantity in coal and oil gas, which it undoubtedly is not. This, I think, is purely a question of temperature; the fire-clay gas retort is never above an orange-red, which means 800° to 900°, and the gas inside the retort probably never approaches that temperature. Again, in oil-gas making, 800° would be the outside temperature employed, whilst to convert any large proportion of diluted hydrocarbons into acetylene requires at least 1000°. Indeed, if diluted hydrocarbons are passed through a half-inch tube heated to 1000°, the yield is very small, as only the thin layer in contact with the walls of the tube is raised to the required temperature, and it was for this reason that it was necessary to use so fine a tube in the preceding experiments.

In order to see how temperature affected the amount of acetylene formed during the manufacture of gas, I made separate batches of oil gas from Russian petroleum in a Patterson retort.

Acetylene formed in the Manufacture of Oil Gas.

Oil used—Russian "distillate oil," sp. gr. 0·0864.

Temp. of retort	500°	700°	800°	900°
Yield of gas per gallon, cub. ft.	12	60	72	84
Illuminating power	54·8	50·7	57·1	42
Unsaturated hydrocarbons .	39·13	36·56	36·55	22·40
Acetylene	0·052	0·084	0·38	0·46

Showing that the quantity of acetylene steadily increases with rise of temperature.

The analyses of flame gases made by Landolt (*Ann. Phys. Chem.*, 1856, **99**, 389—417), Blochmann (*Annalen*, **168**, 295), and myself all point to the hydrogen present in the gas burning first, and there is no doubt but that the water vapour so formed and superheated in its passage up the flame interacts with the hydrocarbons, giving hydrogen and carbon monoxide, whilst in the luminous zone the action of water vapour and carbon dioxide upon the incandescent carbon particles again gives rise to the same products, so that their production in reality never ceases until the outer non-luminous zone of the flame is reached.

In this zone it has always been supposed that the presence of a free supply of oxygen caused complete combustion, and that with a properly constructed burner only carbon dioxide and water vapour escaped into the air.

Delicate analyses made and described by me in the *Journal of the Society of Chemical Industry* (1891, **10**, 413) show that this is not the case. Heumann noticed that if a luminous flame was made to spread itself out over a cold surface, luminosity was destroyed, but could be restored by heating the substance over which the flame was playing, and this reduction of luminosity is produced by withdrawal of heat from the flame, the temperature falling below the point necessary for the decomposition, or in some cases even the production of acetylene, and in the outer zone of the flame the inrush of cold air sucked into the flame so cools it as to render it non-luminous, and finally extinguishes it, and if the air and products of combustion be collected close to the flame but not in absolute contact with it, anywhere between 2 inches and 4½ inches above the burner, it will be found to contain small traces of carbon monoxide, acetylene, methane, and even hydrogen. At the extreme tip, however, combustion is more perfect, and only carbon monoxide and minute traces of methane are to be found escaping.

It is usual to describe the structure of flame as built up of four zones, but if any such division into parts be necessary, I think it would be better to found them upon the main reactions taking place, due to the heat generated, and to describe them as three :—

1. The inner zone, in which the temperature rises from a comparatively low point at the mouth of the burner to between 1000° and 1100° at the apex of the zone, and in this portion of the flame the constituents of the gas undergo various decompositions and interactions, which culminate in the conversion of part of the hydrocarbons into acetylene; carbon monoxide and hydrogen being also produced, and passing into the next sphere of action, together with some methane and the products of combustion.

2. The luminous zone, in which the temperature ranges from 1100°

to a little over 1300°; here the acetylene formed in the inner zone becomes decomposed by heat with liberation of carbon, which at the moment of separation is heated to incandescence by its own combustion and by the combustion of carbon monoxide and hydrogen, and gives luminosity to the flame.

3. The extreme outer zone, in which the cooling and diluting influence of the entering air renders a thin layer non-luminous, and finally extinguishes it.

With an ordinary coal-gas flame, this results in the escape of traces of hydrogen, methane, acetylene, and carbon monoxide, whilst with a very rich gas unconsumed carbon also escapes.

This description of a luminous flame is of necessity far from complete, as it leaves out of consideration the numerous subsidiary interactions which are taking place, but I think it gives the general outline of the main reactions.

When Knapp and others first showed that a luminous gas flame could have its luminosity destroyed by mixing the gas before burning with inert diluents, such as nitrogen, carbon dioxide, and steam, it was recognised that the nitrogen in the air was an important factor in rendering such flames as those of the Bunsen burner non-luminous, and most valuable contributions were made to our knowledge of the subject by Landolt, Blochmann, Heumann (*Annalen*, **181** and **182**), and others, but, as far as I know, no quantitative attempt has been made to arrive at an idea of the relative importance of the various factors which influence the combustion of coal gas and the light-giving value of the flame.

In these experiments, I used a Bunsen, fitted with two supply pipes leading into the chamber at the foot of the upright tube, each pipe being connected with a small meter, which was from time to time checked with a standard meter, so that the flow of gas and air could be accurately regulated and measured. Working with this arrangement, the amount of air necessary to render the flame non-luminous was first determined:—

6·0 volumes of gas required 13·5 volumes of air.

13·5 volumes of air contain roughly 2·7 volumes of oxygen and 10·8 volumes of nitrogen, and on now passing coal gas and nitrogen through the burner, at the rate of 6 volumes of coal gas to 10·8 of nitrogen, a flame was obtained which had only a faintly luminous tip, whilst on passing coal gas as before, at the rate of 6 volumes to 2·7 volumes of oxygen, a luminous flame is produced, which flashes back unless the tube is covered with fine wire gauze.

This experiment was then repeated on the photometer.

Bunsen burning gas alone (5 cub. ft. per hour), 5·6 c. p.
,, ,, 5 cub. ft. gas and 2·2 cub. ft. oxygen, 3·1 c. p.
,, ,, ,, ,, 9 of nitrogen, not readable.

It appears from this experiment that the amount of oxygen in the volume of air necessary to destroy luminosity does less than one-half the work, and I then tried the effect of varying the amount of oxygen added, with the following results :—

5 cub. ft. gas alone = 5·6 c. p.
5 ,, gas to 1·1 cub. ft. oxygen = 5·4 ,,
5 ,, ,, 1·5 ,, ,, = 8·0 ,,
5 ,, ,, 2·2 ,, ,, = 3·1 ,, Gauze used.
5 ,, ,, 2·5 ,, ,, = 0·0 ,, ,, ,,

It has been already shown that the amount of nitrogen present in the volume of air required to render the flame non-luminous just falls short of the quantity necessary to bring about the same effect by dilution only, and in order to determine the volume required to entirely destroy luminosity, coal gas was burnt at the rate of 6·2 cubic feet per hour, and was supplied with pure nitrogen, which had to pass at the rate of 14·2 cubic feet per hour before all luminosity disappeared, or practically the same amount of nitrogen is required as of air :—

1 vol. of gas required 2·30 vols. of nitrogen.
1 ,, ,, requires 2·27 vols. of air.

This result at first sight looks as if the oxygen in the air really only acted in the same way as the nitrogen, that is as a diluent ; but if this were so, then mixtures of oxygen and nitrogen, richer in oxygen than air, should only affect the luminosity to about the same extent as air, which is not the case, as is shown by the following results :—

Volumes of Varying Mixtures of Nitrogen and Oxygen required to render 1 vol. of Coal Gas Non-luminous in Bunsen Burner.

Gas.	Volume of mixture required.	Composition of mixture.			Volume of oxygen present in amount required.
		Nitrogen.		Oxygen.	
1 vol. requires	2·30 of	1	to	nil	nil
1 ,, ,,	2·30 ,,	5	,,	1	0·38
1 ,, ,,	2·27 ,,	4	,,	1	0·45
1 ,, ,,	2·02 ,,	3	,,	1	0·50
1 ,, ,,	1·49 ,,	2	,,	1	0·50
1 ,, ,,	1·00 ,,	1	,,	1	0·50
1 ,, ,,	0·50 ,,	nil	,,	1	0·50

This set of experiments shows very beautifully that until the percentage of oxygen reaches the amount present in the atmosphere, the diluting influence of the nitrogen is so strong that it prevents the oxygen having any practical effect in the destruction of the luminosity, but that as soon as the quantity of oxygen present has risen above 25 per cent., then its activity has so far overcome the diluting influence of the nitrogen that the latter has ceased to exercise any retarding influence upon it.

In almost every laboratory it may be noticed that whereas most of the Bunsens are burning with their normal blue, noiseless combustion, some one or two are roaring and burning with a sharply defined green centre, and experiment shows that this is brought about by the gas delivery jet having become partly stopped up, and a far larger supply of air than is necessary to cause non-luminosity being sucked in :—

Ratio of Gas to Air in Blue and Green Non-luminous Combustion.

Blue, 1 vol. of gas to 2·27 of air.
Green, 1 vol. of gas to 3·37 of air.

The green centre shows, therefore, that a large excess of air is passing in, and such a flame is on the point of flashing back in the burner and lighting at the bottom.

In this case, the kind of action taking place in the flame has undergone considerable alteration, the flame being fiercer and smaller than in the normal combustion, the change being due to the fact that the proportion of oxygen to coal gas in the mixture is such that the chemical activity of the oxygen is able to overcome the diluting and cooling action of the nitrogen, so that the latter has practically ceased to act.

The next step was to determine the proportions by volume of various gases required to render the Bunsen flame non-luminous, the number being limited by having to use a wet meter for their measurement.

Volumes of Gases required to render 1 *vol. of Coal Gas Non-luminous.*

1 vol.	of gas	requires	0·5	vol.	of oxygen.
1 ,,	,,	,,	1·26	,,	carbon dioxide.
1 ,,	,,	,,	2·27	,,	air.
1 ,,	,,	,,	2·30	,,	nitrogen.
1 ,,	,,	,,	5·11	,,	carbon monoxide.
1 ,,	,,	,,	12·4	,,	hydrogen.

Showing that a diluent which burns and adds to the general temperature of the flame must be added in far greater quantity than an inert and non-combustible diluent such as nitrogen, a result fully borne out by experience.

Some observers have attributed the varying effect of diluents to the effect of density (D. Waldie, *Phil. Mag.*, 1838), but the destruction of luminosity in a flame can be brought about by cooling as well as by dilution, as is well shown by the experiment described by Heumann (*loc. cit.*).

It is evident that, this being the case, if one diluent has the power of abstracting more heat from the flame than another, it will be more active in reducing the luminosity, and a smaller quantity will be required to render the flame non-luminous. And on comparing the specific heats of equal volumes of the diluents used in the last experiment, the reason for the small quantity of carbon dioxide required is at once seen.

Specific Heats of Equal Volume.

Oxygen	0·2405
Carbon dioxide	0·3307
Nitrogen	0·2370
Air	0·2374
Carbon monoxide	0·2370
Hydrogen	0·2359

If this be the true explanation, then it should be easy to trace the action by the decrease in temperature of the flame when carbon dioxide is used to render it non-luminous.

In order to take the temperatures of the inner cone of the flame by means of the thermo-couple before described, it is manifest that the wires, even when protected by glass, must not be passed through the outer zone, as with mixtures of coal gas and air the heated platinum would set up rapid combination on its surface. To overcome this difficulty, the wires, insulated with glass, were passed up the interior of the burner-tube, and the gas supply was kept constant at 6 cubic feet per hour, whilst the diluents were supplied under pressure at the same rates as before determined, and the results in table, p. 336, were obtained.

These results fully bear out the inferences derived from the behaviour of the flames in the former experiments. In the flames rendered non-luminous by diluents, the inner cone for the first 1½ inches is decidedly cooler than in the luminous flame, owing to the cooling action of the nitrogen or carbon dioxide; in the upper

Temperature of Flame from Bunsen Burner, with Consumption of 6 cub. ft. of Coal Gas per hour.

Point in flame.	Flame rendered non-luminous by			Luminous flame from Bunsen.
	Air.	Nitrogen.	Carbon dioxide.	
½ inch above burner	54°	30°	35°	135°
1½ inch above burner	175	111	70	421
Tip of inner cone........	1090	444	393	913
Centre of outer cone.....	1533	999	770	1328
Tip of outer cone	1175	1151	951	728
Side of outer cone, level with tip of inner cone .	1333	1236	970	1236

portion of the inner cone of the flame rendered non-luminous by air, however, the oxygen of the air is acting, and the temperature is therefore higher than in the luminous flame; whilst, in both, the hottest portion of the flame is almost half way between the tip of the inner and outer cones.

In flames rendered non-luminous by inert diluents, this is not the case, as the full amount of air necessary for combustion only being obtained at the side and tip of the outer cone, these are the hottest points.

The low temperature registered at the tip of a luminous flame is probably due to the impossibility of keeping that portion of the flame steady when the gas is burning from a Bunsen with the air supply closed.

Experiments with a Bunsen burning a mixture of air and coal gas in such proportions as to give the green inner cone showed that although the excess of air caused a low temperature at the bottom of the inner cone, the increase in rapidity of oxidation due to excess of oxygen caused a rapid rise of temperature, and that a hotter and smaller flame was the result:—

	Blue inner cone.	Greenish inner cone.
Tip of inner cone...............	1090°	1575°
Centre of outer cone............	1533	1630
Tip of outer cone	1175	1545
Side of outer cone, level with the tip of inner cone.............	1333	1511

These experiments, as well as the researches of Heumann, show that oxidation, dilution, and cooling all help to bring about the destruction of luminosity in a Bunsen flame.

At this point it seemed important to determine how dilution acted towards gases richer than ordinary coal gas; in order to do this, I decomposed Russian distillate oil in a "Patterson" retort, and made two batches of oil gas, one of 24-candle power, the other of 43-candle power.

These gases were then analysed with the following results:—

Oil Gas.

	24 c. p.	43 c. p.
Carbon dioxide..........	0·95	1·52
Oxygen	0·74	0·00
Unsaturated hydrocarbons.	18·06	33·16
Saturated hydrocarbons ..	43·62	45·15
Carbon monoxide	0·95	0·52
Hydrogen................	34·58	19·65
Nitrogen................	1·12	0·00
	100·00	100·00

The gases were then tested in the Bunsen burner, at a carefully regulated rate of flow, with air, carbon dioxide, and nitrogen, and gave the following figures:—

Amount of Diluent required by 1 *vol. of Gas to render a Bunsen Flame Non-luminous.*

Gas.	Candle power.	Air.	Nitrogen.	Carbon dioxide.
Coal gas	16·3	2·27	2·30	1·26
Oil gas	24·0	5·38	4·20	2·29
Oil gas	43·0	7·86	4·71	3·12

These figures reveal the interesting fact that with a rich gas far less nitrogen than air is required to bring about loss of luminosity, on account of the high temperature produced by the combustion of the heavy hydrocarbons with the oxygen in the air. The effect of the inert diluents was also noticeable, as at the point of non-luminosity the flame separated itself $\frac{3}{4}$ inch from the mouth of the burner, and became very elongated.

The question now arises as to how dilution, apart from its cooling action, reduces the luminosity.

On passing 1·5 cubic feet of coal gas slowly through a platinum tube, 0·15 metre long and 12 mm. in diameter, packed with platinum foil and heated to redness by a Bunsen burner, it deposited 0·2200 gram of carbon. The same volume of gas was then diluted with 3·3 cubic feet of nitrogen, and the experiment repeated under exactly similar conditions, when only 0·0013 gram of carbon was deposited, dilution reducing the amount of decomposition to this enormous extent. A second experiment was then made in which, by means of a blow-pipe flame, a higher temperature was obtained, and 1·5 feet of gas, as before, was passed through the tube, when it deposited 0·2780 gram of carbon.

	Gas before heating.	After heating.
Carbon dioxide	0·2	0·8
Oxygen	0·3	0·2
Unsaturated hydrocarbons	4·2	3·0
Carbon monoxide	2·6	2·8

whilst, under the same conditions, a mixture of 1·5 cubic feet of coal gas and 3·45 cubic feet of nitrogen deposited 0·0640 gram of carbon, showing that the effect of dilution is decreased by increase of temperature.

These experiments, I think, show that when coal gas is diluted to the degree necessary to give a non-luminous flame in the Bunsen burner, the liberation of free carbon is reduced by the retarding action of the inert gas, but as the temperature rises this action gets less and less.

The action of diluents in increasing the temperature necessary to bring about deposition of carbon was, I believe, first noticed by Wartha, and is probably due to two distinct causes. As has already been shown, the formation of acetylene from the hydrocarbons in the gas is retarded by dilution, whilst if any be formed the temperature necessary to decompose it into carbon and hydrogen is greatly increased.

These two retarding influences give time for the oxygen present in the air introduced with the gas, and in the air sucked into the flame, to burn up the hydrocarbons without previous decomposition, and so prevent luminosity, and it is probable that the prevention of the formation of acetylene is the chief factor, as only the merest trace can be detected in a non-luminous Bunsen flame. Collecting the results, we can now explain the various actions which lead to loss of luminosity as follows:—

1. The chemical activity of the oxygen introduced in the air, which causes loss of luminosity by burning up the molecules of hydrocarbons before, in their diluted condition, they can form acetylene.

2. The diluting influence of the nitrogen which increases the temperature necessary for the formation of acetylene from the hydro-

carbons, whilst if any be formed a higher temperature is necessary for its decomposition. In this way diluents alone will render a flame non-luminous, and in the normal Bunsen flame nitrogen acts in this way until the hydrocarbons have been destroyed by oxidation.

3. The cooling influence of the air introduced, which is able to add to the general result, although the cooling is less than the increase in temperature brought about by more rapid oxidation.

4. In a normal Bunsen flame, the nitrogen and the oxygen are of about equal importance in bringing about non-luminosity, but if the quantity of air be increased the oxidation becomes the principal factor, and the nitrogen practically ceases to exert any influence.

I should have liked to have worked out the secondary reactions taking place in a luminous flame, and so have completed this paper; but, as Professor Smithells proposes to undertake this, I leave the question in his hands, and trust that he may be successful in clearing up the many points which remain to be solved.

In conclusion, I wish to express my thanks to my assistants, Messrs. F. B. Grundy and H. S. Marsh, for the help they have given me in the work entailed in this paper.

XXVI.—*Physical Properties of Solutions of some Metallic Chlorides.*

By S. SKINNER, M.A., Demonstrator at the Cavendish Laboratory, Cambridge.

THE dissolution of substances in water alters the properties of the latter in different ways; in some cases, the effects can be explained by van't Hoff's hypothesis, but in the majority they do not agree with it, and require some further hypothesis, that of dissociation (Arrhenius), or that of combination with the solvent (Mendeléeff). The following experiments show that in some cases alcohol behaves like water, which is its chemical analogue.

The first property observed is the variation of the boiling point, and as this is not an easy determination for solutions, the method used will be briefly described. The solution, after being heated to a temperature just short of its boiling point, is raised and maintained at that temperature by blowing through it the vapour of the solvent, which is boiled in a separate vessel. This method of heating overcomes all surface difficulties; for, even when glass vessels are used, water indicates with an immersed thermometer bulb the same temperature as the steam above it to within 1/50th of a degree, the limit to which my thermometer could be read. When alcohol was used as the solvent, the escaping vapour was led into a wide Liebig's condenser. With a view to test the working of this arrangement, some experiments were made with watery solutions, the results of which agreed with those of previous observers. For comparison, in the following tables the boiling points of watery solutions are given, quoted, when not freshly determined, from Gerlach's exhaustive work.

Mercuric Chloride.

In water.		In ethyl alcohol.	
Per cent.	B. p.	Per cent.	B. p.
4·8	100·10° C.	10·0	78·43° + 0·52
9·0	100·16 ,,	19·4	78·43 + 0·95
11·04	100·20 ,,	—	—
15·2	100·275° C.	—	—

Mercuric chloride, as far as I know, does not form crystalline compounds with either of these solvents.

Mercuric Cyanide.

In water.	
Per cent.	B. p.
6·62	100·11°
19·10	100·29

Calcium Chloride.

In water.		In alcohol.	
Per cent.	B. p.	Per cent.	B. p.
5·6	101°	6·705	78·43° + 0·70°
10·3	102	11·5	,, + 1·45
14·5	103	16·85	,, + 2·70
17·5	104	24·3	,, + 5·20
20·0	105	—	—

Graham has described a compound $2CaCl_2,7C_2H_6O$, but later experimenters state that it is $CaCl_2,4C_2H_6O$. With water, it forms $CaCl_2,6H_2O$.

Lithium Chloride.

In water.		In alcohol.	
Per cent.	B. p.	Per cent.	B. p.
3·38	101°	2·4	78·43° + 0·70°
6·54	102	5·39	,, + 2·15
13·04	105	8·01	,, + 4·18
16·66	107	9·93	,, + 5·55
19·35	109	15·94	,, + 11·75
21·8	111	—	—

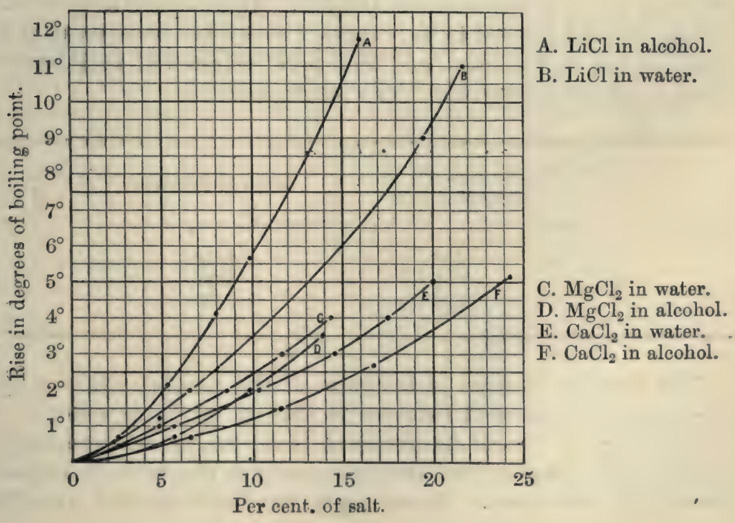
Lithium chloride forms with water $LiCl,2H_2O$; with alcohol, $LiCl,4C_2H_6O$. The curve for aqueous solutions is fairly expressed by $y = Ax + Bx^2$, where $A = 0·24$, and $B = 0·0109$; whilst for alcoholic solutions, $A = 0·146$, $B = 0·047$.

Magnesium Chloride.

In water.		In ethyl alcohol.	
Per cent.	B. p.	Per cent.	B. p.
4·6	101°	5·56	78·43° + 0·73°
8·4	102	8·53	,, + 1·34
11·6	103	9·62	,, + 1·77
14·3	104	13·84	,, + 3·54

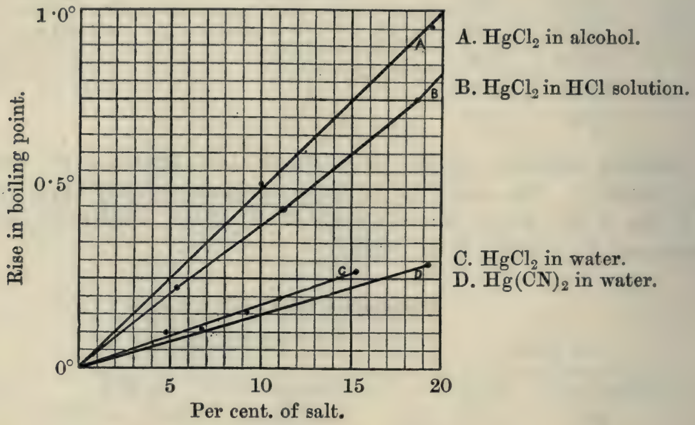
This forms compounds $MgCl_2,6C_2H_6O$ and $MgCl_2,6H_2O$. These results are shown in Diagrams I and II, and a glance is sufficient to

DIAGRAM I.



recognise the difference in the character of the effect of mercuric chloride and of the other salts mentioned. The effects of the same salts are alike in water and in alcohol.

Diagram II.



The nature of a mercuric chloride solution has been examined by a second method. Henry's law for the distribution of a gas between a space and a solvent can be applied to the case of a substance in solution in two solvents which do not mix. Mercuric chloride is soluble in ether, and ether only dissolves slightly in water. Experiments were therefore made to find its law of distribution between these two solvents in the presence of one another. Aqueous solutions of various strengths were allowed to be in contact with ether for some days at the temperature of the room, and then equal volumes of each layer were drawn out and evaporated. The results were :—

Per cent. of salt in aqueous layer.	Ratio of division.
1·4	4·12
2·1	4·37
5·9	4·00

The ratio of division is the ratio of the mass of salt in a certain volume of the ethereal solution to that in an equal volume of the aqueous layer. It will be observed that the last solution was some four times stronger than the first, and yet the ratio of division is practically the same. Experiments by Berthelot and Jungfleisch

(*Ann. Chim. Phys.* [4], **26**, 396) show that this ratio varies very rapidly for solutions which are good electrolytes, such as tartaric acid, for which the ratio is $133 - 8\,p$, p being the number of grams of acid in 10 c.c. of the aqueous solution.

This coefficient is constant on the assumption that the salt behaves as a gas in solution in two different solvents.

A mercuric chloride solution in alcohol or in water differs very considerably in its specific electrical resistance from solutions of other salts. It is not far removed from that of distilled water. The following measurements are by Mr. T. C. Fitzpatrick (*Phil. Mag.*, 1887); K is the conductivity at 15°.

$\frac{1}{20}$ equivalent in grams dissolved in 250 c.c. of solvent.		K.
$HgCl_2$	water	0·0000655
—	alcohol	0·000000803
$MgCl_2$	water	0·00817
—	alcohol	0·000587

If hydrochloric acid be boiled under constant pressure, it becomes stronger or weaker until it reaches a definite strength corresponding to that particular pressure. This was experimentally examined by Dittmar and Roscoe, who found that the acid prepared in this way behaved like a homogeneous liquid. Mercuric chloride is readily soluble in hydrochloric acid; further, Ditte and others have prepared crystalline compounds of it containing hydrochloric acid.

Some ordinary hydrochloric acid was distilled until the thermometer standing in the vapour became steady at 107·63°, under a pressure of 765 mm. The receiver was then changed, and about a litre of acid passing over at that temperature was collected. This was used as the solvent in the following boiling point determinations, which were made in the way described at the beginning of this paper:—

Mercuric Chloride.

In constant boiling HCl. Per cent.	B. p.
5·6	107·63° + 0·22°
11·3	,, + 0·43
18·5	,, + 0·75
24·2	,, + 1·08

These observations are shown in Diagram II.

In a note on the compressibility of solutions (*Phil. Mag.*, July, 1891), I have remarked that this property varies with the strength of the solution in a manner similar to the different cases described in this paper. We may summarise these cases into two groups, *a*, one in which the measure of the property is a simple function of the quantity of salt present; and, *b*, one in which the measure of the property depends on some higher power. Finally, it should be noticed that alcoholic solutions of many salts, $CaCl_2$, $MgCl_2$, $ZnCl_2$, LiCl, for example, have similar properties to the aqueous solutions of the same salts. This is contrary to Ostwald's statement (*Solutions*, English edition, p. 188), where he says that solutions of salts in alcohol are normal.

XXVII.—*On Limettin.*

By William A. Tilden, D.Sc., F.R.S.

In a paper read to the Chemical Society, nearly two years ago (Trans., 1890, **57**, 323), Mr. C. R. Beck and I described, under the name *limettin*, a substance obtained from the fruit of the lime. The original specimen of raw material having been exhausted, I applied to Mr. Joseph Sturge, a director of the Montserrat Company, and he kindly supplied me with a considerable quantity of the deposit filtered from oil of limes after delivery in this country. This material, which presented the colour and aspect of butter, was much cleaner than the dried deposit first operated upon and, though saturated with the essential oil, was more easily purified.

A small portion of it purified by crystallisation, first from alcohol rendered alkaline by the addition of potash, and subsequently from pure methylated spirit, was found to melt at 146—147°. The melting point of the specimen described in the former paper was 121°. Hence, though the analyses given were closely concordant, the question arose whether the substance first examined was a mixture of two closely allied substances, or whether it was merely contaminated with a small quantity of impurity which brought down the melting point. The appearance of both specimens was the same. In the first series of experiments, the limettin, supposed to be pure, was found to be converted by boiling with pretty strong caustic alkali into a substance having the same appearance and general properties, but melting at 147°, and this was supposed to be deacetyllimettin. It now turns out, however, that this is the pure limettin itself.

To test this question, 18·46 grams of the original substance, which after the whole had been fused in the air-bath was found to melt at 123°, was boiled for about 20 minutes with 54 grams of caustic soda and 150 c.c. water. The alkaline yellow solution was then precipitated with hydrochloric acid, and the whole of the precipitate carefully collected, washed, and dried. It weighed 18·29 grams. The mother liquors were found to contain mere traces of acetic acid, together with a small quantity of a sticky, brown matter soluble in ether. The treatment with soda, therefore, does not extract an appreciable amount of anything from limettin, but it renders the latter more easily capable of purification, for after crystallising the recovered substance, once from glacial acetic acid (which retained a little brown matter) and twice from methylated spirit, it melted at 147—148°. After recrystallisation, it melted sharply at 147·5°.

Hence it appears that the original limettin, melting at 121—123°, was contaminated with a small quantity of a substance which is altered by heating with caustic alkali, but is precipitated from the solution by acids, along with the real limettin. This contamination probably consists of a kind of vegetable wax, of which some quantity was separated in the course of the crystallisations, and which seems to be soluble to about the same extent as limettin in all the solvents, alcohol, acetic acid, toluene, &c., which are available.

The waxy matter separated as far as possible from limettin melts below 100°.

The new supply of raw material was treated in the following manner:—It was first steam-distilled as long as oil came over. The residual yellow mass was semifluid, but solidified on cooling. It was then treated with successive small portions of boiling methylated spirit, and the undissolved crude limettin purified by crystallisation from benzene or toluene, and again from alcohol. The yellowish, waxy matter is very difficult to remove, but even when quite pure, limettin is not white. It crystallises in prisms, or tufts of needles, which are of a pale-straw colour. It is easily soluble in hot alcohol, acetic acid, benzene, or toluene, but dissolves very sparingly in water or in light petroleum. Weak solutions of the pure substance in alcohol, acetic acid, toluene, or water exhibit a strong violet fluorescence, the appearance of which is good evidence of its purity, as the fluorescence is masked completely by the presence of a very small quantity of the attendant yellow substance.

Two combustions of the new substance crystallised from alkaline alcohol, and from toluene, gave the following results:—

Exp. No.	Substance analysed.	CO_2 obtained.	H_2O obtained.	Carbon per cent.	Hydrogen per cent.
1....	0·2924	0·6815	0·1339	63·54	5·06
2....	0·2922	0·6814	0·1337	63·58	5·06
	Mean percentages			63·56	5·06

With the view of studying the structure of limettin, among other experiments tried, a cold alkaline solution was treated with successive doses of potassium permanganate. When an excess of the oxidising agent is used, abundance of oxalic acid and a very little acetic acid is formed, and nothing else. With a smaller quantity (25 grams of permanganate in 800 c.c. of water to 50 grams of limettin and 50 grams of potash in 200 c.c. of water), only brown tarry matters were formed, but a quantity of limettin remained unoxidised. This, when crystallised from alcohol, gave at first, and while the solutions were still brown, brilliant leaflets or scales totally different in aspect from pure limettin. But in proportion as the impurity was removed, the substance recovered, its usual form of pale-yellow prisms (m. p. 147°), the solutions of which exhibited the characteristic fluorescence.

The presence of a very small quantity of the brown product of oxidation seemed to cause a complete change of crystalline habit.

After this treatment, the limettin was deemed very pure, and was, therefore, analysed. The following are the results :—

Exp.	Substance.	CO_2.	H_2O.	C p. c.	H p. c.
3	0·3008	0·7029	0·1343	63·73	4·95
4	0·3013	0·7080	0·1359	64·05	5·01
5	0·1328	0·3092	0·0560	63·48	4·67
6	0·2011	0·4671	0·0850	63·35	4·69
		Mean percentages		63·65	4·83

These numbers agree with the results of the first two combustions.

When melted limettin is heated, it boils at about 200°, a considerable quantity distilling unchanged, even under ordinary atmospheric pressure. That it is unchanged is shown by its characteristic fluorescence, and by the melting point remaining unaltered, provided it is carefully recrystallised. In the former paper, the distilled product was supposed to contain about 1 per cent. more carbon, but the following analyses of the carefully purified substance show that this was an error due to imperfect purification :—

Exp.	Substance.	CO_2.	H_2O.	C p. c.	H p. c.
7	0·2268	0·5310	0·1005	63·85	4·92
8	0·2241	0·5224	0·1007	63·57	4·99
9	0·2342	0·5464	0·1049	63·63	4·97
		Mean percentages		63·68	4·98

The mean results of the two series of combustions quoted in the former paper were—

Carbon	63·14 and 63·29
Hydrogen	4·86 and 4·71

The substance analysed was, as already explained, not quite pure. The three series of analyses of the pure compound give the percentages as stated above, namely:—

Exps. ..	1—2.	3—6.	7—0.
Carbon	63·56	63·65	63·68
Hydrogen	5·06	4·83	4·96

The formula adopted on the results of the old analyses was $C_{16}H_{14}O_6$. But there appears now to be no doubt that the composition of limettin is really expressed by the formula $C_{11}H_{10}O_4$, which corresponds equally well with the results of experiment:—

	Calculated for	
	$C_{11}H_{10}O_4$.	$C_{16}H_{14}O_6$.
Carbon	64·07	63·57
Hydrogen	4·85	4·63

Determination of Molecular Weight.

I. Depression of freezing point of acetic acid:—

Limettin taken	0·8579
Acetic acid...........	103·6161

Freezing point of acetic acid..........	3·120°
„ solution............	2·970
Depression	0·150

$$K = 39,\ M = \frac{39 \times 0{\cdot}8579 \times 100}{0{\cdot}15 \times 103{\cdot}61} = 215.$$

II. Depression of freezing point of benzene:—

Limettin taken	0·7815
Benzene „	85·609

Freezing point of benzene............	1·560°
„ solution............	1·350
	0·210

$$K = 49,\ M = \frac{49 \times 0{\cdot}7815 \times 100}{0{\cdot}21 \times 85{\cdot}609} = 213.$$

The formula $C_{11}H_{10}O_4$ gives the molecular weight 206.

Action of Bromine on Limettin.

When into a cold solution of limettin in benzene a solution of bromine in benzene is allowed to fall, drop by drop, an orange-coloured precipitate is formed so copiously that the liquid often becomes semi-solid. After an excess of bromine has been added, the precipitate shrinks, and becomes paler in colour. Hydrogen bromide is immediately evolved. In order to prepare the bromo-derivative, the solution of limettin in benzene, toluene, or glacial acetic acid is poured into a solution of bromine in the same solvent, keeping the bromine throughout in excess. The precipitate is allowed to remain, in the presence of a slight excess of bromine, for about half an hour, and is then filtered off and crystallised from chloroform. It is very slightly soluble in spirit of wine. The bromo-compound is never quite white; it forms scales or small prisms.

Analysis.

Preparation 1.—Toluene used as solvent:—

0·2337 gram gave 0·2468 gram AgBr = 44·94 per cent. Br.

Preparation 2.—Acetic acid as solvent:—

0·3589 gram gave 0·3706 gram AgBr = 43·95 per cent. Br.

Preparation 3.—Acetic acid as solvent:—

0·3411 gram gave 0·3486 gram AgBr = 43·49 per cent. Br.

A portion of Preparation 2 was dissolved in chloroform, bromine added, and the mixture heated in a sealed tube for about six hours at 120—130°, and the product analysed.

0·3406 gram gave 0·3590 gram AgBr = 44·81 per cent. Br.

Under the most favourable circumstances, therefore, the compound contains not more than 44·8 to 44·9 per cent. of bromine, and this agrees closely with the number calculated from the formula $C_{11}H_8Br_2O_4$, which requires 43·95 per cent. of bromine. This point required careful examination, because it was found that chlorine produces *tri*-chloro-substitution compound at once.

Three other specimens of the bromo-compound were submitted to combustion, and gave the following results:—

	I.	II.	III.	Calculated for $C_{11}H_8Br_2O_4$.
		(With silver coil in front.)		
Carbon	36·85	36·59	36·75	36·23
Hydrogen ..	2·64	2·74	2·91	2·19
Bromine ...	—	—	43·23	43·95

The bromo-compound melts at 257° with decomposition.

Action of Chlorine on Limettin.

Limettin was dissolved in glacial acetic acid and dry chlorine passed into the cold solution. A precipitate was at first formed which redissolved in presence of an excess of chlorine. After standing for some hours, the addition of water threw down a white precipitate, which was washed and crystallised from boiling methylated spirit, in which it was found to be more soluble than the bromo-derivative.

First Preparation.

Exp.	Substance.	AgCl.	Percentage of Cl.	Mean.
1	0·2055	0·2846	34·25	—
2	0·0850	0·1189	34·58	34·41

Second Preparation.

	Substance.	CO_2.	H_2O.	C p. c.	H p. c.
3	0·2533	0·3930	0·0548	42·24	2·40

The formula $C_{11}H_7Cl_3O_4$ requires—

Carbon	42·64
Hydrogen	2·26
Chlorine..............	34·40

The chloro-compound crystallises in perfectly white, silky needles. It melts at 188·5°.

Action of Chlorine on Dibromolimettin.

The dibromo-compound suspended in glacial acetic acid is treated with excess of chlorine in the cold. The bromo-compound dissolves, and on addition of water, after some time, a mass of colourless, crystalline needles is deposited. After recrystallisation from toluene, the new compound melted at 202°.

0·1355 gram substance gave 0·1737 gram of mixed bromide and chloride of silver.

The amount required by the formula $C_{11}H_7Br_2ClO_4$ is 0·1766. Probably, therefore, the replacement of the third atom of hydrogen by the chlorine was not quite complete, but the result is sufficiently near to establish the nature of the compound.

Action of Oxidising Agents on Limettin.

A 5 per cent. solution of chromic acid oxidises limettin completely into carbon dioxide and acetic acid. The action of permanganate has already been described (p. 346).

Nitric acid produces a red, resinous substance, which, by further action of the strong acid, dissolves, and a pale-yellow solution, containing abundance of oxalic acid, results. Dilute nitric acid (1 vol. of acid of sp. gr. 1·4, diluted with eight times its volume of water) slowly attacks limettin when gently heated. Effervescence, due to escape of carbon dioxide, continues for some time, and a yellow precipitate is formed. This precipitate, filtered off and dissolved in boiling methylated spirit, gives tufts of small, yellow prisms, amounting to about 30 per cent. of the limettin employed.

Analysis.

Substance.		CO_2.	H_2O.	C p. c.	H p. c.	N p. c.
0·2917	gave	0·5657	0·1003	52·86	3·80	—
0·2950	,,	0·5733	0·0983	52·98	3·70	—
0·3170	,,	15 c.c. N_2 at 19°; bar. 750·5 mm. =				5·4
0·2226	,,	11·6 c.c. N_2 at 20°; bar. 749·1 mm. =				5·9

These results correspond with the formula of a mononitro-limettin, $C_{11}H_9(NO_2)O_4$, which requires

Carbon	52·54
Hydrogen	3·60
Nitrogen	5·53

Action of Caustic Potash on Limettin.

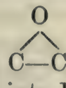
As explained in the former paper (*loc. cit.*, p. 325), limettin fused with potash gives phloroglucol with acetic acid and a little formic acid. No other acid has been detected, although the proportion of alkali and the time and temperature of fusion have been varied.

Action of Hydriodic Acid on Limettin.

Hydrochloric acid, even at 160°, produces no volatile alkyl chloride, but when limettin is boiled with about 10 times its weight of hydriodic acid of sp. gr. 1·96, it evolves methyl iodide readily. 2 grams of limettin boiled with the acid, and the evolved vapour conducted first up an inverted Liebig condenser, which was allowed to become warm, and then into a bulb-tube kept at a temperature below 0°, gave 2·37 grams of the methyl iodide.

On the assumption that one methoxyl group is present, 2 grams of limettin should yield 1·37 grams of methyl iodide. It is, therefore, evident that two such groups are present. This hypothesis requires 2·75 grams of methyl iodide.

Action of Hydrating Agents.

Much diluted hydrochloric or sulphuric acid has no effect on limettin. Potash dissolved in methyl alcohol, heated with limettin at 150°, leaves the greater part of it unchanged. The solution yields very little acetic acid, and sufficient phloroglucol to produce a purple colour upon a slip of deal wood. Moderately strong sulphuric acid gave the best results. 10 grams of limettin were heated to boiling for a few minutes with a mixture of 30 c.c. sulphuric acid and 30 c.c. water. The orange-coloured solution was poured into about 400 c.c. of water, and boiled for some time. The liquid gives a purple colour to deal moistened with hydrochloric acid. On cooling, the orange-coloured, resinous precipitate was filtered off, and the filtrate extracted with ether. The ethereal extract dissolved in a little alcohol mixed with water, and filtered from resin, gave, on standing, a small crop of prismatic crystals. A few more were obtained by dissolving the orange resin in alcohol, and proceeding in the same way. The total yield, however, was very small, probably not more than a gram altogether. As it was necessary to economise, the new substance was not submitted to combustion, but was purified, as far as possible, by recrystallisation, and the product, which was nearly white, was heated at 100° with acetyl chloride in a sealed tube. On opening the tube, there was abundant escape of hydrogen chloride, and on evaporating the excess of the liquid, a residue was obtained which crystallised from alcohol in small, colourless, brilliant prisms. To determine the acetyl in this compound, it was dried over H_2SO_4, and 0·74 gram was boiled with 25 c.c. of 5 per cent. aqueous potash for about 20 minutes. The solution was then carefully distilled with dilute sulphuric acid, the distillate neutralised with pure barium carbonate, filtered, and the solution evaporated to dryness. The residual barium acetate, after drying at 139°, weighed 0·648 gram, and after treatment with sulphuric acid, gave 0·588 gram of barium sulphate. These results correspond respectively to 29·4 per cent. and 29·3 per cent. of acetyl C_2H_3O. The formula $C_{11}H_{10}(C_2H_3O)_2O_5$ requires 29·7 per cent. It is, therefore, the diacetyl derivative of the hydroxy-compound formed from limettin by the addition of the elements of 1 mol. of water. As stated in the former paper, acetyl chloride has no action upon limettin itself, and acetic anhydride with zinc chloride causes blackening. Hence, limettin contains no hydroxyl, but probably includes the group  $C\overset{O}{—}C$, which, by the action of sulphuric acid and water, is converted into HO·C—C·OH.

Limettin is not altered by phenylhydrazine. When boiled with alcoholic potash and excess of ethyl iodide for about five hours, a sticky, brown resin was formed, but the greater part of the limettin remained unchanged. It, therefore, seems to be established that this compound contains no :CO group in any form corresponding to a ketone or an acid.

Limettin in alcoholic solution is unchanged by the action of sodium amalgam. It gives no coloration with ferric chloride.

Conclusion.

The evidence afforded by the results of the experiments described in this paper leads to the conclusion that limettin does not agree with any known compound. It has been shown to have the molecular formula $C_{11}H_{10}O_4$, which may be dissected in the following manner:—

$$C_6H_3\left\{\begin{array}{l}(OCH_3)_2\\C_3HO_2\end{array}\right. .$$

It behaves as a saturated compound, and, therefore, the structure of that part of the molecule which is represented above by the symbols C_3HO_2, is not at present clear, but further experiments are begun, with the object of clearing up this point.

In conclusion, I desire to express my obligations to Mr. J. H. Wilson and to Mr. J. H. Millar, students in the laboratories of the Mason College, for the greater part of the analytical work required in this investigation.

Mason College, Birmingham,
February 12, 1892.

XXVIII.—*On the Search for a Cellulose-dissolving (Cyto-hydrolytic) Enzyme in the Digestive Tract of certain Grain-feeding Animals.*

By Horace T. Brown, F.R.S.

In a recent paper by myself and Dr. G. H. Morris (Trans., 1890, **57**, 497), it was shown that during the germination of the seeds of the grasses the vegetable cell-membrane, constituting the walls of the starch-containing cells of the endosperm, is attacked and dissolved by a cellulose-dissolving, or cyto-hydrolytic, enzyme. This enzyme is secreted by a special layer of cells constituting the epithelium of the scutellum, and the destruction of the cell-membrane which it brings about in the endosperm is a necessary preliminary to the action of the diastase which is secreted by the same cells, and which, owing to its highly colloïdal nature, can only gain access to the reserve-starch after the cell-tissue is broken down.

Although the cell-membrane forming the wall of the starch-containing cells is, in most of the Grasses, very thin, it nevertheless constitutes a most formidable barrier to the passage of the extremely non-diffusible diastatic enzyme which is secreted by the embryo. The same high degree of indiffusibility also holds good with regard to the amylolytic enzymes of the *saliva* and the *pancreas*, for when thin sections of wheat, barley or rye (or, better still, the endosperm-cells of these seeds separated by maceration) are digested at 40° with highly active amylolytic solutions derived from animal saliva or pancreatic secretion, I have always found that the starch-granules contained in the cells whose walls are intact resist the action of the enzyme for a very considerable time, in some cases even for days, whilst, on the other hand, if the cell-wall is ruptured, the enzyme gains ready access to the starch, which it completely dissolves in a very few hours.

A consideration of these results, and of my previous observations on the processes of animal digestion, led me to anticipate that in those cases where an animal is able quickly and readily to digest the uncooked starch-contents of grain, there should be found in their economy some provision for removing the investing cell-membrane and bringing the contained starch-granules and proteïds within the sphere of action of the amylolytic and proteolytic enzymes of the digestive tract.

The digestion of raw, unaltered starch takes place, as is well known, after the contents of the stomach have passed through the pylorus into the small intestine, for little or no action on the starch-granules can be detected until after they have been flooded with the mixed biliary and pancreatic secretions.*

When a *pig* which has been fasted for 48 hours is fed with barley-meal from three to four hours before death, and the contents of various portions of the duodenum are examined, it is found in all cases that scarcely a trace of the original parenchymatous cell-walls of the barley-endosperm can be recognised. The starch-granules, which are being rapidly and visibly acted on by the pancreatic secretion, *are all free from their cell-envelopes*, the endosperm of the grain being in fact as completely broken down and disintegrated as it is under the action of its own embryo during the natural processes of germination.*

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* It is true that the mixed saliva of some animals has a very marked amylo-hydrolytic power, especially on starch which has been previously gelatinised, but its action in the case of ungelatinised starch must be very feeble indeed during the short period of mastication, and its power in this direction must be quickly arrested by the natural acids of the stomach. In the case of some animals, notably the horse, the mixed saliva possesses no starch-transforming power. (F. Smith, *Veterinary Journ.*, No. 156, 1888.)

It seemed of considerable interest to ascertain if this well-marked dissolution of cellulose, and consequent exposure of the starch to the action of the digestive enzymes, could be in any way referred to the secretion of a cyto-hydrolyst by any portion of the digestive tract or by the secretory organs connected therewith, or if it is due to other causes.

The general question of the digestibility of cellulose by animals has not lacked workers, of whom may be mentioned Hofmeister, Henneberg and Stohmann, Schmulewitsch, and Tappeiner, but the work of most of these observers is much diminished in value by the fact that no care was taken by proper antiseptic treatment to differentiate the action of micro-organisms from that of the soluble enzymes. This objection does not, however, apply to the work of Tappeiner (*Zeit. Biol.*, 1884, **20**, 52, 215; *ibid.*, 1888, **24**, 105), which is by far the most important contribution to the subject. Tappeiner sets himself to answer the following questions:—

1. In what section of the digestive canal does the dissolution of cellulose take place?

2. Is it brought about by organisms or by an enzyme?

In attempting to answer these questions experimentally, the contents of the particular part of the digestive canal under experiment were divided into three portions.

(*a*) was boiled in order to destroy both organised and unorganised ferments. (*b*) was kept for some time under as nearly as possible the natural conditions of the contents of the digestive canal, so as to allow the natural digestive and fermentative processes to continue. (*c*) was treated with antiseptics (chloroform or thymol), so as to prevent the action of the organisms, but not that of the enzymes.

These experiments were made upon cows fed with hay, the contents of (1) the first stomach, (2) the middle of the small intestine, and (3) the cæcum and neighbouring parts of colon being removed for examination.

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* The thick cell-walls of the so-called aleurone-layer (Kleberschicht) remain intact in the small intestine, but of the cell-walls of the starchy portions of the endosperm only mere vestiges remain, and these for the most part consist of the older portions of the endosperm-tissue, which lie on the ventral side of the grain, in close proximity to the funiculus. It is just these portions of the cellular tissue which resist for the longest time the solvent action of the cyto-hydrolyst during germination, and when sections of the grain are submitted to the action of the cyto-hydrolyst *in vitro*.

The cellulose in the partially digested food was determined by boiling successively with 1 per cent. solution of sulphuric acid, 1 per cent. solution of caustic potash, and, lastly, washing with alcohol and ether.

Tappeiner concludes from his experiments that there is a certain amount of dissolution of cellulose in the first stomach of ruminants, and that organisms are concerned in this; whether an enzyme also plays any part is left uncertain. The small intestine appears to play no part in the dissolution of cellulose, but in the large intestine cellulose is dissolved concurrently with a fermentation produced by organisms.

This work of Tappeiner, interesting though it is, as throwing light upon the digestibility and nutritive value of more or less lignified cellulose, does not, on examination, help us to any conclusion as to the dissolution of the thin, soft, parenchymatous walls of the endosperm of the Grasses. The dissolution of these cell-walls is of little or no importance to the animal economy from any direct nutritive value which they possess, but their removal, as we have seen, is of the highest importance indirectly.

I have already stated that the *post-mortem* examination of the contents of the duodenum of a pig, killed when in full digestion of a feed of barley-meal, clearly indicates that the cell-walls of the grain endosperm are already dissolved by the time the food reaches this portion of the digestive tract. My attention was consequently first directed to the *pancreas*, as it seemed somewhat probable that this great seat of starch and proteid-dissolving enzymes might also be instrumental in secreting the cellulose-dissolving enzyme of which I was in search.

I have examined the pancreas of *pig*, *horse*, *ox*, and *sheep*, the gland being in each case derived from perfectly healthy animals, and in some cases when the processes of digestion were in full activity, that is, at a time when it would be almost certain that the gland was secreting everything of which it was capable.

Extracts* were made by digesting the finely comminuted gland for several days in chloroform water, and filtering off the clear liquid. This filtrate was examined for a cytohydrolyst by immersing in it thin sections of the endosperm of barley, and observing the cell-walls from time to time under the microscope. Various temperatures were employed for the digestions, ranging from 15° to 40°, but although the starch granules of the sections were all sooner or later dissolved by the amylo-hydrolyst of the animal extracts, not the slightest evidence could ever be obtained of any action on the cell-walls themselves.

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* My warmest thanks are due to Mr. Baden Benger for kindly undertaking to prepare for me these extracts of pancreas, and also some of the extracts of the mucous membrane of stomach mentioned later on.

These experiments were repeated so frequently, and with so many variations, as to leave no room for doubt that amongst the several digestive enzymes secreted by the pancreas we certainly cannot number one having the power of dissolving parenchymatous cellulose.

In the year 1880, I pointed out (Brown and Heron, *Proc. Roy. Soc.*, 1880, 394) that certain portions of the small intestine possess the power of secreting hydrolysing enzymes, but the necessity of examining this portion of the digestive tract, and the biliary secretion, for a cellulose-dissolving enzyme was rendered unnecessary by my discovering that the breaking down of the cell-walls has already taken place *before the stomach-contents have passed through the pylorus.* It was in the stomach itself therefore, or in the salivary glands, that the search had now to be continued.

Mixed human saliva, although so intensely active on starch, was found to be quite powerless to effect any change in the cell-membrane of sections of *barley*, *potato*, *carrot*, *turnip*, *&c.*, both in the cold and at 40°. It seemed, however, quite possible that a cyto-hydrolytic action might be found in the saliva of a grain-feeding animal, and yet be absent from the saliva of man, who has for so many ages taken most of his starch-containing food in a cooked form.

In order to test this, a quantity of the mixed saliva of the *horse* was obtained by the subcutaneous injection of a small quantity of pilocarpine.

When digested with barley sections, which are particularly well suited for experiments of this class, no trace of action on the cell-walls could be detected, the times of digestion varying from 7 hours to 7 days, and the temperatures from 28° to 40°.

As the mixed saliva of the horse is slightly alkaline, and as both the cyto-hydrolyst and diastase have their action intensified in a very slightly acid medium, a further experiment was made after rendering the saliva very faintly acid with formic acid, but here again the results were entirely negative.

It is pretty evident it is in the *stomach* itself that we must search for the cause of the dissolution of the cell-membrane of the starch-containing cells of the ingested grain.

That it is important to the animal economy that this should be the seat of action is rendered clear by the consideration that the proteolytic ferment or ferments which are secreted by the peptic glands are, like the amylolytic enzymes, capable of traversing thin cell-membranes only with extreme slowness, and although it may not be a matter of importance that the *starch* shall be completely liberated at so early a point in the passage of the food through the body, yet it cannot be a matter of indifference to have the *proteïd* portion of the cell-contents brought into intimate contact with the peptonising secretions, so that the whole of the proteolytic work may not be left to the pancreatic secretion.

My observations and experiments, as regards the contents of the stomach, have all been made upon the *horse* and the *pig*, the food in the case of the first-mentioned animal being *oats*, and in the case of the second coarsely ground *barley-meal.*

The horses were in all cases healthy animals which had died or had been destroyed from accidental causes, and which had been fed at a determinate time before death. The stomach-contents were generally placed at once in alcohol.*

An experimental method was possible with regard to the pigs, which were killed in the ordinary way for food, full facilities being afforded for feeding the animals at any desired time before death, and in any desired manner.

The observed disappearance of the cell-membrane during primary digestion may be due to one or more of the following causes :—

1. To mechanical disintegration brought about by the "churning" and "propulsive" movements of the stomach during digestion.

2. To the action of the natural acids of the stomach, which may bring about the dissolution of the cellulose either (*a*) by direct hydrolysis, or (*b*) by converting a zymogen of the grain into an active cyto-hydrolyst.

3. To the action of a special enzyme secreted by some portion of the mucous membrane of the stomach.

4. To the direct or indirect action of living *micro-organisms*. These may break down the cell-wall by—

(*a*.) A direct attack of the living organism without the intervention of a secreted enzyme :

(*b*.) A previous secretion by the organism of a special cyto-hydrolyst :

(*c*.) An indirect production of a cyto-hydrolyst by the modification of some of the constituents of the grain by the vital processes of the micro-organisms.

N.B.—This latter case would be analogous to the intensification of diastatic power in an aqueous extract of barley, when this is submitted for a few hours at 30° to the action of ordinary yeast (*vide* Brown and Heron, Trans., 1879, **35**, 653).

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* I must here express my great indebtedness to Professor Fred. Smith of the Army Veterinary School, Aldershot, for frequently placing at my disposal material derived from the *post-mortem* examination of horses, and for the collection of the horse saliva to which reference has already been made.

5. To the self-digestion of the food under the influence of a cyto-hydrolyst pre-existent in the grain before ingestion.

It now becomes necessary to examine these various possible cases in detail, with a view to determine the *vera causa* of the disappearance of the cell-membrane.

1. That the destruction of the cell-wall is not brought about mechanically by the "churning" of the partially fluid contents of the stomach is abundantly proved by every specimen of the stomach-contents which I have examined. The cell-membrane is dissolved without previous mechanical disintegration, and all the consecutive stages of dissolution can be traced microscopically, commencing with a slight swelling of the cell-wall, and an increased visibility of its stratification, and terminating with the complete disappearance of the minute spindle-shaped fragments into which the cell-wall is resolved. These phenomena are, in fact, exactly similar to those which have been described as occurring during the disappearance of the cell-walls in germination (Brown and Morris, Trans., 1890, **57**, 468).

2. The acids of the stomach are certainly not instrumental in dissolving the cell-membrane, as is proved by the following facts:—A pig which had been fasted for 54 hours was fed with barley-meal 3½ hours before death. The partially digested meal, on microscopical examination, showed that the parenchymatous cell-walls of the barley-endosperm had already been completely dissolved. The stomach-contents, on filtration, yielded a filtrate which was intensely active in dissolving cellulose, as indicated by the complete disappearance within a few hours of the cell-walls of barley sections immersed in it.* This filtrate had an acidity equal to 0·11 per cent. HCl, but since, after boiling, it completely lost its power of attacking cellulose, it is sufficiently evident that its activity as a cyto-hydrolyst was in no wise due to the acid it contained.

I have found that a 0·2 per cent. solution of HCl, which is, I believe, the maximum amount of acidity of gastric juice, does not hydrolyse the cell-membrane of the endosperm of the grasses at 38° to 40°. At most, the cell-walls, after a considerable time, show slight signs of swelling up, but no dissolution takes place.

Although the evidence is so strongly against the stomach acids having any cyto-hydrolytic effect, it was considered desirable to ascertain if the conditions mentioned in 2(*b*) could bring about any such result, that is, if the acids of the stomach could have an indirect influence by converting any one of the food constituents of the nature of a *zymogen* into an active cyto-hydrolyst, a fact which has not been altogether unsuspected in the history of the analogous enzyme starch-diastase.

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* It must be understood throughout this paper that all such experiments were conducted with antiseptic precautions, either chloroform or thymol, usually the former, being employed.

An aqueous extract of a raw barley which was absolutely devoid of any cyto-hydrolytic power was digested at 38° for 20 hours with 0·12 per cent. of HCl, that is, with an amount of acid about equal to that of the stomach-contents. The aqueous extract so treated was found after the digestion to be as free from any cellulose-dissolving power as it was before such treatment.

3. I have made a very large number of experiments on the stomach of the pig in order to ascertain if any positive evidence can be obtained of the secretion of a special cellulose-dissolving enzyme by any part of the mucous membrane. At the outset it was found impossible to prepare a filtered aqueous infusion of the comminuted mucous membrane of the stomach having the slightest action on cellulose, no matter whether these infusions had been made with neutral chloroform-water, or with chloroform-water to which 0·1 per cent. of acetic or hydrochloric acid had been added.

As it had been observed during an investigation upon the hydrolytic enzymes of the small intestine (Brown and Heron, *Proc. Roy. Soc.*, 1880, p. 399) that far more pronounced hydrolytic effects can be obtained from the comminuted tissue itself than from its aqueous infusion, a new series of experiments was commenced in which the mucous membrane of the stomach was previously rubbed up with clean quartz-sand and water to which chloroform had been added. The test sections of barley endosperm were subsequently immersed directly into the turbid infusion so prepared, the digestions being carried on afterwards at temperatures varying from 28° to 40°.

Similar infusions were also made with glycerine, these being largely diluted with water prior to testing for their action on cellulose.

Since there is a considerable difference in size, shape, and structure between the peptic glands of the pyloric and cardiac ends of the stomach, a difference which is probably indicative of some variations of function, care was taken to prepare infusions of the mucous membrane from *both* these regions of the stomach. Moreover, as the activity of the peptic glands is greatest while the processes of digestion are in full progress, in some of my experiments the animals were killed and the dissection made within a short time of their being fed.

In all the numerous experiments, varied in every possible way, *absolutely no evidence could be obtained of the secretion by the mucous membrane of the stomach of an enzyme capable of producing those phenomena of cellulose dissolution which are so well marked in the stomach-*

contents of a grain-fed animal within a short time of the ingestion of food.

4. At first sight it did not seem at all improbable that the dissolution of the cellulose might be brought about either directly or indirectly by the micro-organisms present in all the stomach-contents which I have hitherto examined. I have already signified the three possible ways in which such organisms may be supposed to act.

The microbes of the stomach have been investigated, in the first place, by De Bary (*Archiv für exp. Pathologie und Pharmacologie*, **20**, 243), and more recently by Abelous (*Recherches sur les Microbes de l'Estomac.* Paris, 1889). The general conclusions arrived at by Abelous are that the micro-organisms do not for the most part exercise an important action upon the food in the stomach, where the conditions for their multiplication and functioning are unfavourable, owing, in the first place, to the short time the food remains in the stomach, and in the second place to the acid reaction of the stomach-contents. It is only when the chyme passes into the intestine that the full effect of these micro-organisms begins to be felt.

Amongst the numerous organisms described by Abelous, the *Bacillus butyricus* (*Clostridium butyricum*) stands out pre-eminently as a destroyer of cellulose. As I found this organism fairly abundant in the stomach-contents both of the pig and of the horse, I originally had the intention of preparing pure cultures of this bacillus for purposes of experiment upon cellulose, but this was rendered unnecessary by the unmistakable results afforded by the mixed cultures.

We have already seen that when a pig has been fed with barley-meal, the acid-filtrate from the semi-fluid contents of the stomach is strongly cyto-hydrolytic. It would appear probable, therefore, that if this action is due either directly or indirectly to the multiplication of micro-organisms, we ought to be able to imitate the phenomenon *in vitro* by inoculating a mixture of barley-meal and water with the mixed stomach organisms and incubating at a suitable temperature; taking care, of course, to employ a barley which does not, in the first instance, possess any cellulose-dissolving power.

The following experiment was consequently made:—A Californian barley, the aqueous infusion of which was absolutely without any action on cellulose, was coarsely ground and mixed with cold water at the rate of 100 grams of the meal to 250 c.c. of water. This "mash," after inoculation with a few drops of the washings of the mucous membrane of the stomach of a recently-killed pig, was digested at 36° for 20 hours.*

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* In anticipation of the production of a cyto-hydrolyst under the influence of the organisms, another portion of the "mash," or clear liquid as the case might be, was always digested alongside with the addition of a little chloroform. If the por-

On examination at the end of that time, the mash had acquired the strong disagreeable odour peculiar to the contents of an animal's stomach when digestion is in progress, and differing in a marked degree from the pure butyric odour evolved from a mash simply infected with the organisms naturally adherent to the exterior of the grain.

The fermenting mass was swarming with the bacilli, bacteria, and micrococci of the stomach, but, notwithstanding that these organisms were much more abundant than is usually observed in stomach-contents, *the cell-walls of the endosperm of the grain were still intact, and the filtrate from the mixture possessed no power of dissolving parenchymatous cellulose*, in both these respects differing very much from the stomach-contents of an animal recently fed with barley-meal.

When a freshly-prepared aqueous extract of barley (prepared, of course, from a proved non-cyto-hydrolytic grain) was sterilised and inoculated in the same manner with a few drops of the washings of a stomach, the liquid, as the organisms multiplied, also acquired the characteristic smell of animal digestion. When thin sections of barley endosperm were immersed in this liquid teeming with the mixed stomach-organisms, no action on the cell-membrane could be detected until several days had elapsed. After continuing digestion for five days at 40°, some little action was perceptible, but it proceeded with extreme slowness. The slight action observed in this case was evidently due to a direct attack of the organisms on the cell-wall without the secretion of a soluble enzyme, for the action was at once arrested by the addition of a trace of chloroform. The phenomena have nothing in common with those observed during animal digestion.

I have repeated these experiments many times and in various ways, employing in some cases slightly acid solutions, in order to imitate more closely the natural processes of digestion. The results are uniformly consistent, and clearly indicate that the disappearance of parenchymatous cellulose during the early stages of animal digestion is not due to the intervention of micro-organisms. It is true that certain of these micro-organisms, especially *Clostridium butyricum*, have the power of slowly attacking cellulose, but the time which they require to produce any appreciable result in this direction, and the difficulty they experience in reproducing themselves in an acid medium, such as the contents of the stomach, render it in the highest degree improbable that they exert the smallest influence upon the parenchymatous cell-wall whilst the food remains in the stomach.

tion without chloroform became cyto-hydrolytic, whilst that to which chloroform had been added remained without action on cellulose, it is evident that in the former case the action could only be attributable directly or indirectly to organisms.

5. By a process of exhaustion we have arrived at the only remaining explanation of the destruction of the cell-membrane during digestion, that is, that it is dissolved in the stomach by *a cyto-hydrolyst pre-existent in the grain before ingestion.* I was for some time unprepared to accept this as a full explanation of the facts, but direct experiments have fully confirmed the view, and that none of the other possible causes which I have cited contribute in any degree to the observed results.

It was stated in a recent paper by myself and G. H. Morris (*loc. cit.*), that the cellulose-dissolving enzyme which is of so much indirect importance to the plantlet during the germination of the seeds of the Grasses is not pre-existent in the seed during its resting stage, but is a product of the germinative processes. Now, although this is strictly true as regards the morphologically perfect and highly matured Californian barley which was used during the greater part of that research, I find that it is not strictly true of *all* barley or Grasses, especially of much of the barley grown in this country under somewhat imperfect climatic conditions.* This, as a rule, contains, even in its resting state, a very appreciable amount of cellulose-dissolving enzyme.

The presence of the enzyme in these cases is demonstrable in the cold-water extract of the grain, and its influence in self-digestion of the cellulose is often distinctly noticeable when the coarsely ground meal is digested with water at 35—40° for a short time.

I have also found evidence of the existence of a cyto-hydrolyst in *rye*, but of all grain hitherto examined it is most abundant and most active in *oats*, an aqueous infusion of raw oats being, in fact, much more strongly cyto-hydrolytic than an extract made from an equal weight of air-dried barley malt. This great cellulose-dissolving activity of oats fully explains a fact which I have often observed during the progress of this enquiry, namely, the extraordinary rapidity with which the endosperm of the oat is disintegrated in the early stages of digestion in the stomach of the *horse*, a disintegration which is mainly due to the complete disappearance of the cell-membrane of the grain endosperm.

It seems to me that the very high estimation in which oats are held as a food-stuff may be distinctly correlated with their richness in the cyto-hydrolyst, which enables the reserve substances enclosed in the endosperm cells to come readily under the influence of the digestive secretions.

In order to determine if the whole of the cyto-hydrolyst in the animal stomach is due to self-digestive action of the food-stuff, or if the animal by secretory processes contributes towards the result something which cannot be imitated *in vitro*, the following experiments, which may be regarded as crucial, were instituted.

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* As a rule, those barleys which are grown under the most perfect conditions of climate contain the least cyto-hydrolyst in their resting state.

Two pigs, A and B, which had been fasted for three days, in order to ensure a complete emptying of the stomach, were fed as follows:—

A. With a coarsely ground meal derived from a *barley which had been proved to be perfectly free from any cellulose-dissolving enzyme.*

B. With the same meal as above, with the addition of 10 per cent. of an air-dried barley malt, which was, of course, highly cytohydrolytic.

After the lapse of three hours, both animals were killed and their stomach-contents were at once examined.

In A the barley-meal presented exactly the same appearance as when first administered to the animal. The coarse fragments of endosperm were still tough and unaltered, and under the microscope it was seen that the cell-walls had suffered no dissolution.

The stomach contents of B, on the other hand, presented a totally different appearance. Very few fragments of the starchy endosperm were intact, and the few which were still coherent showed a marked softening and tendency to fall to pieces. Under the microscope the cell-walls were seen to be to a great extent destroyed, the cell-contents being liberated and disintegrated.

This experiment conclusively proves that the animal itself, besides affording a favourable temperature, a suitable mixture of fluid, and plenty of mechanical movement, does not contribute to the dissolution of the cell-membrane, which is wholly brought about by the *enzyme pre-existent in the grain.* When this special cellulose-dissolving enzyme is absent from the food, no dissolution of the cell-wall occurs in the stomach.

There can be no doubt, as regards the experiments just described, that the stomach-contents of animal B would enter the small intestine in a condition far more ready to be acted upon and absorbed than would the stomach-contents of animal A.

The relative value of malted and unmalted barley as a food for stock has been the subject of a long investigation at Rothamsted, and the results were embodied in an elaborate report to the Board of Trade by Sir John B. Lawes, in the year 1866. These results, which are consistent with those obtained in 1845–46 by Drs. Thomas and Robert Dundas Thomson, conclusively indicate that with cows, oxen, sheep, and pigs, "a given weight of barley is more productive, both of the milk of cows and of the increase in live weight of fattening animals, than the amount of malt and malt-dust that would be produced from it" (Report, p. 33), but it is further stated that common experience seems to show that a certain amount of malt is beneficial when given in admixture and in change with other food to young and weakly animals, or in "making up" or "finishing" for exhibition or sale.

The *condimental value* of malt, when used in small quantities as an addition to the food of sheep or horses, has also more recently been insisted upon by Mr. Frederic Beard (*Journ. Roy. Agricult. Soc.*, **17**, 86, 1881).

From the results of the observations I have recorded in this paper, it seems in the highest degree probable that the presence of a cytohydrolyst, and its amount, in the food of grain-feeding animals may be a factor, and perhaps a very important one, in their nutrition; for the more or less complete preliminary preparation of the food in the stomach cannot be a matter of indifference to the animal physiologically. This being the case, the favourable results obtained in certain feeding experiments by the addition of a small quantity of malt as a condiment for the first time receive an adequate explanation.

The malt employed by Mr. Beard had been dried at a temperature not exceeding 100° F., and must consequently have been highly cytohydrolytic and able readily to produce a complete solution of the cell-walls, a solution which appears to be so essential a preliminary to the transformation and assimilation of the cell-contents, both in the vegetable processes of digestion as they occur during the germination of seeds, as well as in the analogous digestive processes which occur in the alimentary tract of animals.

XXIX.—*The Volumetric Estimation of Mercury.*

By Chapman Jones.

Having need of a more rapid process for the estimation of mercury than the usual gravimetric methods, I naturally turned to the use of potassium cyanide, as described by J. B. Hannay (*J. Chem. Soc.*, 1873, **26**, 565). This process takes advantage of the fact that ammonia produces no precipitate in a solution of mercuric cyanide, and consists in rendering the neutral mercury solution turbid by the addition of ammonia, and then adding a solution of potassium cyanide until the turbidity is removed. The mercury present is proportional to the potassium cyanide necessary.

R. V. Tuson and E. Neison (*J. Chem. Soc.*, 1877, ii, 679) have somewhat modified this process in order to make it more readily applicable to acid solutions of mercury salts.* They find that the amount of ammonium salts present must not exceed from 10 to 15 times the weight of the mercury compound, as much ammonium salt prevents the precipitation by ammonia. But sulphates, nitrates, chlorides, or acetates of potassium or sodium may be present to 1000 times the weight of mercury salt without interfering with the reaction. Their general method, therefore, consists in dissolving the mercury compound in acid, as may be convenient, adding a little ammonium chloride, and then potassium carbonate, until an opalescent precipitate appears. The cyanide solution is then added as before. They give experiments showing the trustworthiness of the process as applied to the nitrate, sulphate, acetate, oxalate, sebate, and citrate of mercury; and state that the presence of nitrates, sulphates, chlorides, acetates, oxalates, citrates, and butyrates of potassium, sodium, calcium, and magnesium, and organic matter as far as tested, does not interfere with the accuracy of the method.

From my experience, I cannot affirm that these methods of working are satisfactory. There is considerable uncertainty as to the end of the reaction, because less potassium cyanide will effect a clearance if longer time is allowed. Hannay himself finds this to be the case, and suggests limiting the time, between the addition of the final drops, to one minute. Tuson and Neison suggest half a minute. Less than this would be useless, as the precipitate is tardily dissolved by the cyanide. But I find that such a time limit is not satisfactory, as the precipitate is not always equally soluble in the cyanide; it is liable to differ in its state of aggregation. Nor is it possible to keep it down to a mere opalescence, for, as Hannay observes, if but little ammonia is added, the cyanide increases the precipitate until about half the necessary quantity has been added. I have found variations to the extent of about 1 per cent. from this cause.

On applying the variation of Tuson and Neison to acid solutions of mercury, a smaller quantity of cyanide cleared the solution. The deficiency was generally about 5 per cent., but in one case it was no less than 30 per cent. The suspicion that this anomaly was due to the presence of carbonic anhydride was confirmed by the following observations:—By boiling out the carbonic anhydride from the last-mentioned solution, and allowing it to stand for a short time, a precipitate settled down, which, however, adhered to the flask, so that it was not practicable to titrate it with more cyanide. On boiling off the carbonic anhydride before titrating, the normal amount of cyanide was required. On the other hand, on passing a current of carbonic anhydride into a solution left turbid because of the addition of an insufficiency of potassium cyanide, a large amount of clearing action was observed. The addition of potassium bicarbonate also had a clearing effect.

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* In their paper they recommend the preparation of a solution of potassium cyanide containing 17 grams to the litre. This is evidently a misprint, as 7 grams gives a solution of about the required strength. The figure 17 is reproduced in the fourth and fifth editions of Sutton's *Manual*. I have not been able to see a copy of the sixth edition.

These difficulties and uncertainties can, I find, be entirely eliminated, and the process reduced to a series of operations which are comparatively simple and rapid, by performing the titration in an entirely different manner from either variation suggested by the authors referred to. I employ a solution of mercuric chloride containing 0·01 gram of metal per cubic centimetre, and a solution of crystallised potassium cyanide made by dissolving 7 grams to the litre, the exact value of which is found by titrating it against the mercury solution. Strong ammonia diluted to ten times its bulk, and some diluted to fifty or a hundred times its bulk, are convenient.

If the mercury solution is not fit for titration, the metal is precipitated as sulphide, which, after washing, is washed off the filter and allowed to subside; the clear water is then decanted off, and aqua regia added to the moist residue. The precipitate, with the paper it is on, might doubtless be treated direct with aqua regia, as Tuson and Neison found that organic matter, so far as they tried it, does not influence the result. To avoid the possibility of volatilising the mercury salt, the aqua regia is allowed to act in the cold. In a few hours, sometimes in far less time, the residue is of a pure yellow colour, and the solution may be diluted and filtered. The solution, or an aliquot part of it, is then coloured distinctly with litmus extract, treated with successive small quantities of powdered potassium carbonate until alkaline, warming but slightly, and then rendered just acid with dilute hydrochloric acid, with subsequent boiling to remove the carbonic anhydride. The mercury is not precipitated at all, unless the carbonic anhydride is boiled out before acidification. After cooling, the dilutest ammonia mentioned above is added, a drop at a time, until the litmus in the solution shows that the excess of acid is very slight, or in just insufficient quantity to produce a permanent precipitate. A quantity of cyanide solution, which is known to be in excess of that required, is added, and, as a guide for the first titration, the ammonia may be added until a slight precipitate is produced, and cyanide until the solution is cleared. Two or three drops (not more) of the 1 in 10 ammonia are introduced, and then more of the mercury solution is added until the permanent turbidity produced matches that obtained by adding 0·1 c.c. of the mercury solution to about the same bulk of water as the test, and containing approximately the same amounts of litmus and free ammonia. Each drop of the mercury solution added produces its maximum turbidity in a few seconds, and it can be seen at a glance, if the flasks are properly placed, whether this turbidity is equal to or less than the standard. In a few seconds more it is quite obvious whether the turbidity is permanent or is growing less. Too much free ammonia causes the precipitate to clot together, and so vitiates the result. The presence of the litmus tends, in my experience, to lessen the error due to the variation in the state of aggregation of the precipitate when too much ammonia has been added. The turbidities so obtained will remain apparently unchanged for many hours. The 0·1 c.c. excess of mercury solution is of course allowed for in the calculation.

The following consecutive titrations were done by this method:—

	$HgCl_2$.	KCy.	1 c.c. of KCy = of Hg.
I	16·9	18·1	0·009402
II	18·93	20·27	0·009404
III	19·49	20·93	0·009382

The first two titrations were done with the plain solution of mercuric chloride, litmus only being added. To the third solution, 2 c.c. of concentrated hydrochloric acid and 0·7 c.c. of concentrated nitric acid, were added, and the neutralisation carried out as above. I have almost invariably found that in the presence of alkaline salts rather more cyanide is required, but the difference is practically negligible. About 2 grams of a certain double salt of mercury and silver, containing 52·56 per cent. of mercury, was separated into two parts by a certain reaction, and the mercury in each, after separation from the silver, was titrated in fifths, and a total of 52·22 per cent. of mercury was found.

XXX.—*A Rule for determining whether a given Benzene Mono-derivative shall give a Meta-di-derivative or a mixture of Ortho- and Para-di-derivatives.*

By Professor A. CRUM BROWN and Dr. JOHN GIBSON.

WHEN a monobenzene derivative C_6H_5X is so treated as to give a dibenzene derivative C_6H_4XY, it is well known that, as a rule, this dibenzene derivative is either (*a*) exclusively, or nearly so, a *meta*-compound, or (*b*) a mixture of *ortho*- and *para*- with none or very little *meta-*; and that whether the case shall fall under (*a*) or (*b*) depends on the nature of the radicle X, and not at all, or only very slightly, on the nature of Y.

The first attempt at generalisation on this matter was made by Nölting, who attempted to classify radicles, so that one class should include those the compounds of which, with C_6H_5, give *meta*-di-derivatives, and the other class those the compounds of which, with C_6H_5, give *ortho*- and *para*-di-derivatives. But Nölting's classification, and all the rules derived from it, fail in precision. We cannot apply the rule so as to be quite sure of its meaning. When the rule seems to fail, it is always possible to find an excuse for it. Rules of such a kind are of little use practically or theoretically; they are not really rules, but only indications of regularity.

We have gone over all the cases known to us, and have formulated a rule which holds in all these cases, and is always capable of rigorous application, so that, if in any case it should be found to fail, no excuse could be found for it. We shall best explain our rule by showing how we apply it. We shall write in column A a number of benzene mono-derivatives, in column B the radicles replacing one H of C_6H_6, in column C the hydrogen compounds of these radicles, in column D the hydroxy-compounds of the same radicles, and in column E the letters *m* or *o-p*, according as the mono-derivatives give *meta*- or a mixture of *ortho*- and *para*-di-derivatives.

In column C, we mark with an asterisk those substances which are *not* capable, by direct oxidation, of being converted into the corresponding hydroxy-compounds in the next column, and in column D we mark with an asterisk those substances which can be formed by direct oxidation from the corresponding hydrogen compounds, so that in each horizontal line there is one asterisk and, one only, either in column C or in column D. By direct oxidation we mean oxidation by one step. Thus, no doubt $H{\cdot}CH_3$ can be converted into $HO{\cdot}CH_3$, but not by one step of oxidation; whereas $H{\cdot}CO{\cdot}CH_3$ can, by one step of oxidation, be converted into $HO{\cdot}CO{\cdot}CH_3$. Now it will be seen that wherever the H compound is asterisked, we find *o-p* in column E, and whenever the HO compound is asterisked we find *m* in column E. In other words, when X is naturally to be regarded as a derivative of HX, C_6H_5X gives *ortho*- and *para*-di-derivatives, and when X is naturally to be regarded as a derivative of HOX, C_6H_5X gives *meta*-di-derivatives. Our test by which we determine whether X is to be regarded as derived from HX or HOX is, can HX be directly, by a single oxidising step, converted into HOX or not? If it cannot, then X is to be looked on as derived from HX; if it can, then X is to be looked on as derived from HOX.

A.	B.	C.	D.	E.
C_6H_5Cl	$\cdot Cl$	HCl*	$HOCl$	*o-p.*
C_6H_5Br	$\cdot Br$	HBr*	$HOBr$	*o-p.*
$C_6H_5CH_3$	$\cdot CH_3$	HCH_3*	$HOCH_3$	*o-p.*
$C_6H_5NH_2$	$\cdot NH_2$	HNH_2*	$HONH_2$	*o-p.*
C_6H_5OH	$\cdot OH$	HOH*	$HO\cdot OH$	*o-p.*
$C_6H_5NO_2$	$\cdot NO_2$	HNO_2	$HO\cdot NO_2$*	*m.*
$C_6H_5CCl_3$	$\cdot CCl_3$	$HCCl_3$*	$HO\cdot CCl_3$	*o-p.*
$C_6H_5CO\cdot H$	$\cdot CO\cdot H$	$HCO\cdot H$	$HO\cdot CO\cdot H$*	*m.*
$C_6H_5CO\cdot OH$	$\cdot CO\cdot OH$	$H\cdot CO\cdot OH$	$HO\cdot CO\cdot OH$*	*m.*
$C_6H_5SO_2\cdot OH$	$\cdot SO_2\cdot OH$	$HSO_2\cdot OH$	$HO\cdot SO_2\cdot OH$*	*m.*
$C_6H_5CO\cdot CH_3$	$\cdot CO\cdot CH_3$	$HCO\cdot CH_3$	$H\cdot CO\cdot CH_3$*	*m.*
$C_6H_5CH_2\cdot CO\cdot OH$	$\cdot CH_2\cdot CO\cdot OH$	$H\cdot CH_2\cdot CO\cdot OH$*	$HO\cdot CH_2\cdot CO\cdot OH$	*o-p.*

The table might have been further extended, but these examples are sufficient to show how we apply the rule.

It may be said that $C_6H_5\cdot CCl_3$ gives $mC_6H_5(NO_2)\cdot COOH$. But this is a case in which the experiment cannot be applied, because we have no means of knowing whether the conversion of $\cdot CCl_3$ into $CO\cdot OH$ takes place before or after the replacement of $\cdot H$ by $\cdot NO_2$; and when the experiment can be applied, as in the chlorination of $C_6H_5\cdot CCl_3$, we find that we obtain *o* and *p* $C_6H_4Cl\cdot CCl_3$.

The rule given above is not a *law*, because it has no visible relation to any mechanism by which the substitution is carried out in one way rather than in another way, bnt, if it is found to be rigorously applicable it must be related in some way to a law, and may be of use, both as grouping phenomena together and in guiding us to the cause of the formation of meta-compounds in certain cases, and of ortho- and para- in others.

XXXI.—*Influence of Oxygen and Concentration on Alcoholic Fermentation.*

By Adrian J. Brown.

The following paper describes some experiments which suggested themselves when investigating the effects of varying environment on the reproduction of yeast cells.

In this investigation, I employed the method of direct enumeration of yeast cells by means of a hæmatimeter, after the manner described by Pedersen (*Meddelser fra Carlsberg Laboratoriet*, Hefte I), to whom it was first suggested by Drs. Panum and Hansen. Working in this way, it is possible to determine with considerable accuracy the number of yeast cells present in a known volume of liquid, so that a known number of cells may be introduced into any liquid capable of sustaining their reproductive existence, and at any subsequent time their number can be again ascertained. In experiments on fermentation, this method of determining the yeast by the *number* of cells present, instead of by its *weight* (used by Pasteur and others), has distinct advantages, which are pointed out by Pedersen.

My experiments, amongst other things, tended to confirm our knowledge that, when any fermentable nutritive solution, such as malt wort or a solution of dextrose in yeast-water, is inoculated with a "high" fermentation yeast, and kept at a temperature favourable to yeast growth, the cells reproduce themselves rapidly for a time, and then their reproduction ceases,* and that the fermentation of the solution may still be carried on by the continued life of the cells already formed.

One interesting point in connection with the increase in the number of yeast cells in a fermentable liquid is, that, although different liquids may cause yeast to increase to a differing extent, yet the same liquid, providing all the conditions, such as agitation, &c., are kept constant, appears to cause an increase in the number of cells to about the same maximum, no matter how the amount of yeast added to start the fermentation may vary.†

I quote an experiment to make my meaning quite clear:—

Two flasks, A and B, each containing 150 c.c. of the *same* malt wort, were taken, and to each a different amount of the *same* "high fermentation" yeast was added, so that when the cells were evenly dispersed in the liquids by agitation, $\frac{1}{4000}$ of a cubic millimetre (the standard volume used with my hæmatimeter) of each, contained respectively 0·93 and 7·44 cells. That is to say, one solution contained eight times as many yeast cells as the other at the commencement of the fermentation. The flasks were both kept at a temperature of 25° C. until not only yeast growth, but fermentation also, was quite over, and then the total number of yeast cells present in each experiment was counted. In flask A, the yeast had increased from 0·93 cell to 25·24 in each standard volume; whilst in flask B, 7·44 cells had increased to 27·08. In flask A, the cells had increased to 27 times their original number; whilst in flask B they had only increased

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* These remarks of course only apply to the "primary," or first rapid fermentation of such a liquid as malt wort (such a fermentation in fact, as is carried on in the ordinary process of brewing in England), and do not refer in any way to the "secondary" fermentation and slow yeast increase which takes place in liquids like ale when in cask.

† It is assumed here that the same yeast at the same age is used.

3·6 times, yet the total number of cells found at the conclusion of both experiments was approximately the same, that is, 25·24 in A, against 27·08 in B.

This experiment is one of many which all point to the same conclusion.

There are several points of interest in connection with this question, but I wish at present to confine myself to the fact that the experiments to which I have referred appear to show, that all fermentable nutritive solutions cause "high fermentation" yeast cells to increase in number to some fixed maximum, irrespective of the number of cells originally introduced to start the fermentation.

The experiments described above were conducted by introducing a *less* number of yeast cells into fermentable liquids than these liquids would ultimately develop; I will now give the result of adding more cells.

Two flasks, each containing 100 c.c. of the same malt wort, were taken; to No. I, yeast was added to the extent of 6·0 cells per $\frac{1}{4000}$ c.mm., and to No. II, to the extent of 70·8 cells. After allowing time for complete multiplication of yeast at 24°, the cells were again counted. In No. I, the cells had increased from 6·0 to 24·9; and in No. II, the number of cells found was 68·2, against 70·8 originally introduced.

The number 24·9 found in flask No. I, is evidently the number of cells that the particular wort used would grow; so by adding originally 70·8 cells to flask No. II, this number was far exceeded. As a consequence, there has been *no* increase in the number of cells. The slight decrease is what I have observed in all my experiments with large excess of yeast, and is, I believe, due to a few of the cells dying and becoming disintegrated, so that their attenuated remains are easily overlooked during the process of counting in the hæmatimeter.

During these experiments, the yeast cells were repeatedly examined with the microscope. In No. I, free multiplication of the cells by budding was observed during the early stage of fermentation; but in No. II, not the slightest sign of increase, or growth in size, of the cells could be detected at any time, although the fermentation of the liquid in which they were, proceeded with great rapidity.

In another experiment, carried on at a temperature of 10°, two flasks (Nos. III and IV), each containing 100 c.c. of the same malt wort, were yeasted at the rate of 16·6 and 33·2 cells respectively. After fermentation was over, No. III contained 21·7 cells, and No. IV, 30·45. Here, again, when a number of cells were added exceeding the limit that the fermentable liquid was capable of developing, no increase in the number took place. It is worthy of note that, in this experiment, when the cells in No. IV flask were examined under the microscope at the commencement of fermentation, some of them did show an inclination to increase by budding, but the buds only developed to such a small extent that it was impossible to consider them as complete cells when enumerating the individuals present at the end of the experiment. It will also be noticed that the amount of yeast added was not very largely in excess of the maximum the liquid was capable of developing. Under similar circumstances, this result often occurs, particularly when the fermentation is carried on in malt wort, or is agitated by mechanical means; but when the number of cells added exceeds by two or three times the total number the liquid is capable of developing, it is then rare to observe the slightest sign of budding.

When it is known that a nutritive fermentable solution will only sustain the growth of yeast cells to some fixed point, it is, perhaps, not surprising to find that, if a greater number of mature yeast cells are introduced into such a liquid, there is little or no reproduction. But when this fact is recognised, it appears to open out a method of experimenting on the fermentative powers of yeast in a manner which, I think, has not been attempted before.

Although consideration of the phenomenon of alcoholic fermentation gives rise to difference of opinion amongst chemists and biologists, I think all must agree that, however produced, fermentation is the work of the individual yeast cell itself, and that the fermentation of a liquid, no matter how large its volume, is really the joint action of the active yeast cells present working as individuals. In studying alcoholic fermentation, obviously it is necessary in most experiments to consider this phenomenon in relation to the yeast that causes it. When fermentation experiments are carried on under ordinary circumstances, a great difficulty met with is that the yeast itself is not a constant quantity; and although the quantity present at any given time can be determined by weighing or, better still, by counting the cells, yet so many unknown and imperfectly known factors are present, such as the rate at which the cells have been increasing, their fermentative power at different ages, &c., that conclusions drawn from experiments made in this way concerning the relation of yeast cells to their fermentative power, must be peculiarly liable to error.

An ideal method of experimenting would be to take a single non-increasing yeast cell and study its action as the cause of alcoholic fermentation; for, as it has been shown long ago that fermentation can be brought about by yeast cells that are not multiplying, it follows that the factor of yeast increase may be eliminated entirely when studying the fermentative property of a yeast cell, for it is evidently a something apart from its multiplying property. At present, it appears impossible to experiment on a single non-increasing yeast cell in the manner just suggested, but when we know from the experiments described before, that by taking a large number of yeast cells we can cause fermentation without any increase in the number of cells, and when we recognise that the work of a large number of cells is really the *sum* of the work of the individual cells present, it seems probable that experiments on fermentation made under these conditions might yield interesting results, so many complicating factors with regard to yeast increase being removed.

The first experiments made, were undertaken with a view of ascertaining the influence of oxygen on the fermentative power of yeast cells which did not increase in number. To a malt wort of 1065 sp. gr. "high" fermentation yeast was added, so that, when the yeast cells were evenly distributed by agitation, $\frac{1}{4000}$ c.mm. of the liquid contained 85 cells. 120 c.c. of this solution were poured into a flask, A, so as nearly to fill it, and its mouth was closed in such a manner as to allow the carbon dioxide given off during fermentation to escape without air gaining access to the solution. 120 c.c. of the same solution were also poured into a flask, B, of about 1500 c.c. capacity, so that the bottom of the flask was only covered with a thin layer of the liquid. The flask was also arranged so that a current of air could be drawn through the liquid. Two equal quantities of the same liquid containing the same number of yeast cells were thus arranged, so that one, A, should ferment out of contact with the air (excepting the small amount present at the commencement of fermentation), and the other, B, should ferment not only with a large surface exposed to the air, but also with a rapid current of air continually passing through the solution. The fermentation was carried on at a temperature of 19°, and progressed very rapidly, owing to the large amount of yeast present. After three hours, the fermentation was stopped in both flasks by the addition of salicylic acid. The solutions in each flask were then distilled, and from the sp. gr. of the distillates the amounts of alcohol were determined. After correction for the alcohol introduced with the original yeast, the amount of alcohol formed by the fermentation in flask A was 3·35 grams, and in flask B 3·56 grams, showing that fermentation had been carried on by the yeast cells rather more rapidly when aërated than when not so treated.

On counting the yeast cells at the termination of the experiments, it was found that no increase in number had taken place in either case; but microscopic examination showed that a very small percentage of the cells in each flask had developed minute buds, but not nearly large enough to allow them to be considered as complete cells. The number of cells in the aërated flask that showed these minute buds was slightly greater than in the other, and it might be urged that this was the cause of more sugar being decomposed, owing to the presumably greater size of a number of the cells.

Another experiment was undertaken in order to increase the amount of oxygen present during fermentation, and also to avoid even the slight signs of incipient yeast multiplication that took place in the last experiment. In order to attain this last result, the fermentable liquid chosen for experiment was a 15 per cent. solution of dextrose in yeast-water. Such a solution, although it promotes the growth of yeast, does not appear to be quite such a favourable medium as malt wort for this purpose, and consequently overcrowding it with yeast cells more easily prevents all tendency towards multiplication.

50 c.c of the yeast-water and dextrose solution were placed in a tall, narrow cylinder, so that a strong current of air could be drawn through the full depth of the liquid so rapidly that a great part was constantly in a frothy condition. Previously to starting the experiment, yeast was added to the solution to the extent of 90 cells per $\frac{1}{4000}$ c.mm. At the time of starting this experiment, another portion of the same sugar solution, mixed with the same number of the same yeast cells, was fermented in a closed flask out of contact with the air. Both fermentations were carried on at a temperature of 19° for three hours, and then stopped with salicylic acid as before. After determination of the sugar left unfermented in both solutions, by means of the polariscope, it was found that whilst 1·96 grams of dextrose had been fermented in the solution out of contact with air, 2·32 grams had been fermented in the solution through which air had been passing in very large quantities. In neither case did the yeast cells show the slightest signs of budding or enlargement.

This last experiment also seems to indicate that yeast cells submitted to the action of oxygen, so far from their fermentative power being diminished, have it slightly increased. There is a slight objection, however, to both the foregoing experiments, for, whilst the yeast cells have been kept in continual motion in the aërated liquids by the bubbling of the air through them, the cells in the other flasks have been in a comparatively quiescent state, and it is thus possible that the more rapid change of liquid surrounding each cell in the aërated experiment, may encourage a more rapid decomposition of the dissolved sugar by the fermenting organisms, and that this additional aid to fermentation may mask the effect of oxygen on the cell. In order to avoid this possible complication, two more experiments were made, in one of which a solution of dextrose in yeast-water was fermented in a current of air in exactly the same way as the preceding experiment, whilst in the second case the fermentation was carried on in a similarly arranged tube, through which a current of carbon dioxide was passed at about the same rate as the current of air in the other experiment. The same number of yeast cells were added to both solutions (90 per $\frac{1}{4000}$ c.mm.), and the fermentations carried on side by side at the same temperature (23°) for $3\frac{1}{4}$ hours. After stopping the fermentations and estimating the dextrose left undecomposed, it was found that in the 50 c.c. of solution through which the air had passed, 4·28 grams of dextrose had been fermented, whilst in the presence of carbon dioxide only 3·99 grams had disappeared. The yeast cells themselves showed no signs of multiplication in either case.

In these experiments, therefore, we again find that the cells freely exposed to the action of oxygen have decomposed most sugar, although in both cases the agitation of the liquids was similar.

In order to ascertain if the current of carbon dioxide had itself acted as a deterrent agent on the activity of the yeast cells fermenting in its presence, two more experiments were made similar to the last, excepting that a current of hydrogen was passed through the second solution, instead of carbon dioxide. At the termination of these experiments, it was found that the yeast cells in presence of air had decomposed 2·45 grams of dextrose, and those in presence of hydrogen had only decomposed 2·26 grams, whilst the yeast cells in neither case had increased in number or size.

In this case again, we find the continued life of non-multiplying yeast cells, doing most work in the presence of oxygen.

It will be noticed in all the experiments described before, that, owing to the large number of yeast cells of necessity used to carry on the fermentations, this action proceeded with great rapidity and allowed the experiments to be continued through only a short space of time. This is evidently a disadvantage in studying such a phenomenon as the action of oxygen on yeast cells when fermenting sugar, and it may, perhaps, limit the maximum effect that oxygen can have. In order to prolong the action of oxygen as much as possible, advantage was taken of the power which low temperature has, of causing fermentation with yeast to proceed slowly.

To a 10 per cent. solution of dextrose in yeast-water, yeast cells were added to the number of 71 per $\frac{1}{4000}$ of a c.mm. Portions of this solution were placed in two flasks immersed in a water-bath kept at a constant temperature of 7°, and through one solution a current of hydrogen was passed, and through the other a current of air at the rate of about 8 litres per hour. The fermentations proceeded slowly at this low temperature. After 24 hours, during which time about 190 litres of air had passed through the aërated flask, both fermentations were stopped. The yeast cells in neither case showed signs of budding, or increasing in size. The amount of sugar fermented in the hydrogen flask was found to be 4·882 grams per 100 c.c. of the solution, whilst in the air flask, 5·289 grams per 100 c.c. had been fermented. Now decomposition of these amounts of sugar in 24 hours cannot be considered very rapid fermentation, and the air passed through the aërated solution has been very large indeed; yet we see in these experiments, like the preceding ones, that the cells exposed to the influence of oxygen have fermented a little more sugar than those not so treated.

It is well known that M. Pasteur explains the phenomenon of alcoholic fermentation as an action brought about by living yeast cells existing without oxygen, in consequence of which they abstract the oxygen they require from the sugar (molecule ?), and so cause it to split up into alcohol and carbon dioxide.

In discussing this question (*Études sur la Bière*, p. 252), Pasteur states that if yeast is supplied with sufficient free oxygen for all the necessities of its life, it lives after the manner of a mould, and ceases to be a ferment; therefore the ratio between the weight of the plant and the sugar used as food by the plant is similar to that of ordinary fungi. On the contrary, if yeast is entirely deprived of oxygen, its fermentative power is at its highest point, and the greatest disproportion is found between the weight of the yeast and the sugar decomposed. Pasteur further adds, *that if oxygen is present in varying quantities, the fermentative power of the yeast would pass through all the degrees comprehended between the two extreme limits mentioned before.*

In the experiments I have described, in which yeast cells whilst fermenting have been submitted to the action of oxygen, probably in no case can we expect that the cells could take *all* the oxygen they required from the air with which they were supplied, but they would, especially in the latter experiments, be able to take a very large quantity; consequently, from Pasteur's statement last quoted, we should expect distinct evidence of the yeast cells having had their fermentative power arrested considerably. But there are no signs of such action; on the contrary, their power is greater.

As the results of Pasteur's experiments were obtained by weighing the yeast that caused a given fermentation, and not by counting the cells, I repeated two experiments in the same manner as those last quoted, and also estimated the *weight* of the yeast both before and after fermentation, in order to bring my method of experiment into greater harmony with that of M. Pasteur.

In estimating the yeast by weight, a measured volume of the liquid containing it was filtered, and in each case care was taken to wash the collected yeast with the same bulk of chloroform-water. It is advisable to do this in order to get comparative results, because yeast cells yield some of their solid contents to the wash water.

A 10 per cent. solution of dextrose in yeast-water was prepared, to which was added yeast, so that $\frac{1}{4000}$ c.mm. contained 87·6 cells. 100 c.c. of this solution gave on filtering 1·903 grams of dry yeast. The fermentations were carried on in currents of air and hydrogen, as in the preceding experiment, for 23 hours, at a temperature of 9°.

On stopping the fermentations, it was found that 6·20 grams of dextrose per 100 c.c. had been fermented in the hydrogen flask, whilst 7·38 grams had been fermented in the air flask. No increase in the number of cells had taken place. The weight of dry yeast per 100 c.c. from the hydrogen flask was 2·130 grams, and that from the air flask 2·060 grams. It will be noticed that in both cases the yeast is slightly heavier after fermentation, although the number of cells remains the same (possibly this is due to assimilation during fermentation); but the main point to consider is that, at the finish of the fermentations both in air and hydrogen, we have almost exactly the *same weight of yeast* as well as the *same number of cells*. Hence, apparently, whether yeast is estimated by counting the cells, or weighing them, equal amounts of yeast, under the conditions of the foregoing experiments, ferment rather more sugar in the presence of air than when deprived of it.

In the experiments I have described, the results have been arrived at by comparing fermentations carried on side by side, with, and without air, such fermentations being allowed to proceed for an equal length of time. In Schützenberger's work on fermentation (International Series), the author criticised Pasteur's conclusions with regard to the *rôle* oxygen played in alcoholic fermentation, and drew an opposite conclusion from Pasteur's experiments to that of their author. In M. Pasteur's answer to Schützenberger (*Études sur la Bière*, p. 245, *et seq.*), in reiterating his own views and combating those of Schützenberger, he states that "the power of a ferment is independent of the *time* during which it performs its functions." If we take this statement as correct for *all* experiments on fermentation, it might, perhaps, modify the conclusions drawn from the experiments I have described, inasmuch as they were comparative experiments, depending on *equal time* as a chief factor. Although Pasteur's argument is difficult to follow in its entirety, I think there is little doubt that in viewing fermentative power as he does, he looks on it as the total power exercised by a growth of yeast throughout its life history in some fermentable and nourishing liquid, in fact, as a sort of increasing many-celled organism, using sugar in varying ways, according to its age or surroundings (like a growth of *Mucor mucedo*). Throughout my experiments, I have considered fermentation as a product of the "continued life" of a non-increasing individual cell; hence I think, however Pasteur's statements with regard to *time* and fermentation may be applicable to his own method of experiment in which he considered yeast growth *en masse* in relation to the fermentation it accomplished, it is not applicable to mine. My method of experiment is, in fact, analogous to that of M. Pasteur when conducting his investigation into the effect of surrounding fruit with atmospheres of carbon dioxide and air; in this case he worked with the "continued life" of non-multiplying cells for an equal length of time (*Études*, pp. 260—261), and from the results draws the general conclusion that "in short, fermentation is a very general phenomenon. It is life without air, or life without oxygen."

Although the experiments I have described in this paper were originally commenced with the idea of following out and studying the action of oxygen upon fermenting yeast cells according to Pasteur's theory of fermentation, I find myself unable to bring the results into harmony with this theory, and not only is this the case with the experiments just described, but it is so with some experiments undertaken to investigate the fermentative power of yeast cells of different ages. One of these experiments I will describe.

Six flasks were taken, similar in size and shape, each containing 150 c.c. of an 18 per cent. solution of dextrose in yeast water. To the liquid in each flask an equal amount of yeast was added, so that $\frac{1}{4000}$ c.mm. of each solution contained 0·65 cell. All the fermentations were started at the same time, and kept at a constant temperature of 22°.

There were thus six separate solutions similar in every respect; so at any given time the fermentation and yeast growth would be alike in all. Working in this way, it is possible, by taking one flask at any given time, to determine the state of fermentation and yeast growth in the remaining flasks without disturbing them in any way, and so introducing such complicating factors as the effects of agitation, &c., into the calculations.

It must be borne in mind that, in the present experiments, unlike the previous ones, yeast is only used in small quantities, and not in excess; consequently increase in number of the yeast cells by budding takes place.

After the fermentations in all six flasks had proceeded for 12 hours, one flask was taken and fermentation and yeast growth rapidly stopped by the addition of salicylic acid. The number of cells present was then counted, and the alcohol formed by fermentation estimated. At intervals of 12 or 24 hours these operations were repeated on each of the remaining flasks, so that a series of figures were found expressing the amounts of alcohol and the number of yeast cells present in a fermentation at intervals of 12 or 24 hours.

The following table gives these figures, and also others deduced from them, in the manner described at the heads of the columns :—

	A.	B.	C.	D.	E.	F.
	Number of cells found in each experiment.	Mean number of cells present during each interval of time.	Total grams of alcohol found in each experiment in 100 c.c. of the liquid.	Grams of alcohol formed in each interval of time in 100 c.c. of the liquid.	Proportion of grams of alcohol per 100 c.c. to a single cell, in each interval of time.	Interval of time in each experiment.
						hours.
January 9, 11 P.M. .	0·65	—	—	—	—	—
" 10, 11 A.M. .	4·87	2·76	0·654	0·654	0·237	12
" 10, 11 P.M. .	12·03	8·45	1·933	1·279	0·151	12
" 11, 11 A.M. .	15·38	13·70	2·975	1·042	0·076	12
" 12, 11 A.M. .	15·88	15·63	4·237	1·262	0·080	24
" 13, 11 A.M. .	15·80	15·80	6·187	1·950	0·123	24

Column B in the above table gives the *mean* number of yeast cells present during each interval of time between the experimental determinations of the alcohol and yeast. It will be noticed in column A, how rapidly the number of cells has increased during the first 36 hours of fermentation; so in order to compare the number of cells with the alcohol they have formed during each interval of time between the experiments, it is necessary to take the *mean* number of cells present during such time. This I have done by dividing the sum of the cells at the beginning and end of each interval by 2. The result is not quite the correct mean number, because yeast multiplication does not proceed at an even rate, but is most rapid at first, and falls away gradually. The error in the mean number used, however, is too small to appreciably affect the results expressed in column E. In this column is expressed the proportion of the mean number of cells present during a given time to the alcohol formed during the same time, and is arrived at by dividing the weights of alcohol in column D by the mean number of cells found in column B. It will of course be borne in mind that the numbers of cells given, refer to the numbers found in $\frac{1}{4000}$ c.mm., and the weight of alcohol, to the amount found in 100 c.c. of the fermenting liquid, so that the figures in column E are only comparable with each other. From these figures the actual amount of alcohol formed by a single cell can be determined, but it is more convenient to take the numbers given, as the others would be exceedingly small.

After consideration of the numbers given in column E, it is very evident that the cells during the early stage of the fermentation, when they were multiplying most rapidly, were at the same time fermenting sugar most rapidly.

Several other experiments, made with different yeasts and different fermentable solutions, confirm this conclusion.*

It has generally been supposed that fermentation is comparatively slow during the early and multiplying stage of yeast cell life, and that the cause of this is, that the oxygen usually present in a liquid at the commencement of fermentation, whilst aiding the reproduction of the cells at the same time limits their fermentable power, according to Pasteur's theory. But my experiments contradict this idea.

The Rapidity with which Different Strengths of Sugar Solutions are Fermented by Yeast.

The following experiments were made to ascertain the rapidity, or *rate*, at which sugar in solutions of different strengths was fermented by equal numbers of non-multiplying yeast cells.

Five small flasks were taken, each containing 50 c.c. of a solution of dextrose in yeast-water. The amount of sugar in each flask varied in the following manner:—

Flask No.	I.	50 c.c. of a	5	per cent.	solution	of dextrose.
,,	II.	,,	10	,,	,,	,,
,,	III.	,,	15	,,	,,	,,
,,	IV.	,,	20	,,	,,	,,
,,	V.	,,	30	,,	,,	,,

To each flask was added the same number of yeast cells, namely, 90 per $\frac{1}{4000}$ c.mm. The conditions under which the fermentations were carried on were kept the same in every particular. The temperature was 20°, and the time of fermentation $3\frac{1}{2}$ hours. No multiplication of the yeast cells took place. The fermentations were stopped as usual, and the residual sugar estimated by the polariscope. The amount of sugar that had been fermented in each flask was then calculated. The results, expressed as grams of sugar per 100 c.c., are given below:—

No. I (containing a 5 per cent. solution of dextrose), 4·214 grams dextrose fermented.

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* In a paper published in the Transactions of the Laboratory Club (now the Institute of Brewing) on the numerical increase of yeast cells, I refer to some of these experiments more fully (Vol. 3, 1890).

No. II (containing a 10 per cent. solution of dextrose), 5·347 grams dextrose fermented.
No. III (containing a 15 per cent. solution of dextrose), 5·695 grams dextrose fermented.
No. IV (containing a 20 per cent. solution of dextrose), 5·911 grams dextrose fermented.
No. V (containing a 30 per cent. solution of dextrose), 3·264 grams dextrose fermented.

From the above experiments, and others I have made, it appears that an equal number of non-multiplying yeast cells, in an equal time, ferments (approximately) the same weight of sugar in solutions varying in strength from 5 to 20 per cent. When the strength of the sugar solution reaches 30 per cent., there is a marked falling off in the rate at which the sugar is decomposed. There is also a falling off, evident at the 5 per cent. strength, but not to such a marked extent. It should be borne in mind also, when considering this last case, that (according to the conditions of my experiment), during the latter part of the fermentation, the yeast cells would have much less than 5 per cent. of sugar to act upon; indeed, at the termination of the experiment there was only about 0·8 per cent. of sugar left undecomposed.

In a paper on alcoholic fermentation, by Dumas (*Ann. Chim. Phys.*, 1874, **3**, 81), some experiments are described, from the results of which the author concludes that the duration of fermentation is proportional to the quantity of sugar present. This involves the conclusion I have drawn from my experiments with 5 to 20 per cent. solutions of sugar. Dumas experimented with solutions containing less than 4 per cent. of sugar, so the lessened rate of fermentation of strong sugar solutions has not been noticed. It is interesting to note that, in all the experiments described in his paper, Dumas worked with such a large excess of yeast that multiplication of the cells during fermentation can hardly have taken place. Although he has not recognised this fact, the results he got enabled him to conclude "that fermentation of sugar by yeast can be studied like any regular phenomenon which, when subject to determinate disturbing forces, would be able to show their influence with precision." This conclusion of Dumas is in the main upheld by my experiments with non-multiplying yeast cells.

The similarity in the rate with which yeast cells ferment the same weight of sugar from solutions containing such widely different amounts as 20 and 5 per cent. shows that, if *diffusion* is one important factor in fermentation, it cannot be the controlling one, in these cases at least, otherwise the rates of fermentation would be very variable. Bourquelot, in his experiments on the varying rates of fermentation of different sugars (*Ann. Chim. Phys.*, **9**, 245), shows that diffusion plays an important part in the rate of fermentation, but his experiments were made with very dilute solutions of sugar, and it is possible the action of diffusion might be manifest under these conditions, and yet be quite hidden by the more rapid and vigorous fermentations in my experiments; that is to say, if the power of fermentation is exercised within the cell wall, it is possible that the rate of diffusion of sugar in the weakest solution I have used, may be as great as, or greater than, the maximum power of fermentation which the cell is able to effect. However, since the publication of the recent work by Gayon and Dubourg (*Compt. rend.*, **110**, 16), who show that some species of yeast ferment different sugars in entirely different ratios to their diffusibility, Bourquelot's work has lost some of its former importance. An interesting point in connection with the even rapidity of fermentation of sugar in solutions of widely different strengths is, that it is entirely at variance with the ordinary laws regulating chemical change (Vernon Harcourt, *J. Chem. Soc.*, **20**, 460). According to O'Sullivan and Tompson (Trans., 1890, **57**, 865), invertase, in acting upon solutions of cane sugar, is governed by those laws which regulate simple inorganic reactions, and therefore they conclude that vital processes do not enter in any way into the action of this enzyme. If this conclusion is generally applicable, it certainly throws a difficulty in the way of those who think that fermentation itself may be caused by an enzyme, for, as we have seen, fermentation does not appear to conform to the same laws as invertase.

In connection with this question, an attempt was made to trace the action of a constant number of yeast cells on a solution of sugar, and to ascertain at certain intervals of time the rapidity with which fermentation was proceeding in the same solution; in fact, to treat the yeast cells as though they were an unaltering chemical reagent like invertase, with which O'Sullivan and Tompson experimented in a similar manner when they prepared the curve showing its "time action" on cane sugar.

It was recognised, before making the experiments, that yeast could not be expected to act the part of an unaltering chemical reagent in a very exact manner, as the vitality of its non-multiplying cells must become exhausted at some time, to say nothing of the effects that alcohol and other products of fermentation may have on them; it, however, appeared interesting to see how closely the rate of fermentation under these circumstances would agree with my previous experiments in which such disturbing factors could not influence the results to any very large extent.

A solution of dextrose in yeast-water was prepared, containing 12·32 grams per 100 c.c.; to 400 c.c. of this solution, yeast cells were added at the rate of 90 per $\frac{1}{4000}$ c.mm. The fermentation of the solution was conducted at a constant temperature of 23°, and at intervals of an hour, portions of the liquid were removed in order to determine the amount of sugar fermented. Throughout the experiment, the yeast cells showed no signs of budding.

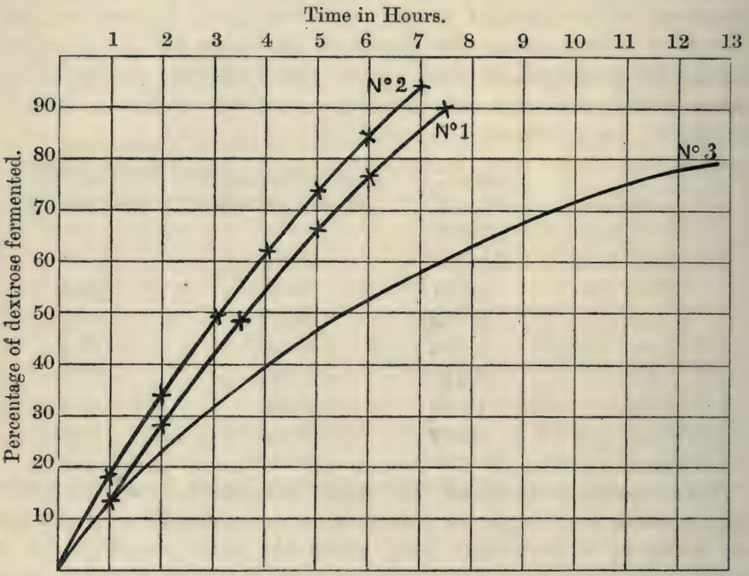
In the following table, the second column shows the amount of sugar per 100 c.c. present in the solution at each interval of time; the third column shows the grams of sugar per 100 c.c. that were fermented during each interval of time; and the fourth column shows the percentage of the sugar fermented during each interval:—

Time.	Dextrose in 100 c.c.	Dextrose fermented in each interval.	Per cent. of dextrose fermented in each interval.
11.0 A.M.	12·320	—	—
12.0 noon	10·157	2·163	17·6
1.0 P.M.	8·191	1·966	33·5
2.0 ,,	6·160	2·031	49·9
3.0 ,,	5·653	1·507	62·1
4.0 ,,	3·211	1·442	73·8
5.0 ,,	1·703	1·508	86·1
6.0 ,,	0·852	0·851	93·0

This experiment confirms the conclusions drawn from my previous experiments, that sugar, in solutions varying from 20 to 5 per cent. in strength, is fermented with about the same rapidity, for we notice in column 3 that in the first three intervals of time almost exactly equal amounts of sugar have been fermented, whilst the fermenting solution itself has varied in strength from 12 to 6 per cent. of sugar. After the third interval of time, there is a falling off in rapidity of fermentation to the extent of about 25 per cent., at which rate it keeps fairly constant until the sugar solution is reduced to the small strength of 1·7 per cent. of sugar.

It appears remarkable that the fermentative power of the yeast cells should have kept to such an even rate of work in this experiment, when not only the sugar on which it was acting varied so much in quantity, but also when other gradually-increasing factors were being introduced, such as the products of fermentation, and the ageing of the non-multiplying yeast cells. Under the conditions of my experiment, these factors evidently cannot exert a very powerful influence on the fermentative power of yeast cells.

I give time curves calculated from this and another experiment conducted in a similar manner, which show how nearly the rapidity of fermentation of sugar solutions of varying strengths, when represented in this way, approach a straight line. For purpose of comparison, I have also added a curve calculated to represent what the action would be if yeast cells fermented sugar according to the ordinary laws of chemical reaction. It will be seen at once how entirely different the two systems of curves are.



Nos. 1 and 2. Time curves of fermentations. No. 1 represents the fermentation of a 16 per cent. solution of dextrose, and No. 2 a 12 per cent. solution of the same.

No. 3. Calculated curve representing decomposition of dextrose according to laws regulating chemical change.

With reference to the very distinct falling off in rapidity of fermentation when the strength of a sugar solution reaches 30 per cent., as such a solution has a high sp. gr. of 1115, it seemed interesting to attempt to find out if it was only the high specific gravity of the sugar solution which checked fermentation. The following experiments were made with this view in mind:—

No. I. A 15 per cent. solution of dextrose in yeast-water was prepared.

II. A solution containing 15 per cent. of dextrose and 15 per cent. of milk sugar.

III. A 30 per cent. solution of dextrose.

No. I solution had a sp. gr. of about 1058, and Nos. II and III a sp. gr. of about 1115; but whilst in No. III the whole of the sp. gr. was due to dextrose, in No. II half was due to dextrose and half to the unfermentable milk sugar.

100 c.c. of each of these solutions were fermented with non-increasing yeast cells in the usual way, at a temperature of 72° F., for 3½ hours. At the termination of the experiments, the dextrose fermented in each flask was determined.

Solutions.	Dextrose fermented in 3½ hours.
No. I (15 p. c. dextrose)..........	7·66 grams
No. II (15 p. c. dextrose and 15 p. c. milk sugar)..............	6·42 „
No. III (30 p. c. dextrose)..........	4·46 „

From these results it appears, that although in No. II the fermentation has been slightly checked by the addition of milk sugar to raise the sp. gr. of the solution, yet the falling off in rapidity of fermentation is not nearly so great as when the whole of the high sp. gr. is due to dextrose, as in No. III experiment. It appears probable, therefore, that the sp. gr. of 30 per cent. solutions of sugar is not the main cause why fermentation proceeds more slowly than with solutions of lower gravity. The results of the foregoing experiments have also been confirmed by experiments with malt worts of high sp. gr., in which the whole weight is not due to fermentable sugars.

XXXII.—COMMUNICATIONS FROM THE RESEARCH LABORATORY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

Contributions to our Knowledge of the Aconite Alkaloïds. Part II. *The Alkaloïds of true* Aconitum napellus.

By Wyndham R. Dunstan and John C. Umney.

The very discrepant observations of various workers as to the number, nature, and properties of the alkaloïds contained in the different species of aconite have been attributed to several sources of error:—

i. To the confusion of different species. It is alleged that it is by no means easy to distinguish between the roots of the different species and varieties, and it is, therefore, highly probable that mixtures of roots have been examined. There is good reason to believe that each species and possibly some varieties contain distinct alkaloïds.

ii. The principal aconite alkaloïds are remarkable for the ease with which they undergo decomposition, especially hydrolysis. Many of the processes hitherto used in extracting the alkaloïds from the plant, as well as those adopted in "purifying" the products, must have led to decomposition of the natural alkaloïds, and it is, therefore, probable that some of the alkaloïds examined and described as constituents of the plant were in reality their decomposition products. The researches of Wright and his fellow workers afforded much valuable information on this point, and led them to the conclusion that "*A. napellus* roots contain as chief active constituent a crystallisable base aconitine, $C_{33}H_{43}NO_{12}$, together with less active amorphous bases probably formed therefrom during extraction." "On examination of the non-crystalline bases, they uniformly furnish numbers quite compatible with the notion that they are formed from the crystallisable bases (of *A. napellus* and *A. ferox*) by saponification, dehydration, polymerisation, &c., changes to which alkaloïds as a class appear to be peculiarly prone" ("The Alkaloids of the Aconites." Part III. Trans., 1878).

iii. A third source of error resides in the circumstance that the determinations of the composition and properties of the alkaloïds have been proceeded with before conclusive evidence of the purity of the material was obtained. The result is that mixtures have been examined and described as single alkaloïds. This source of error is, perhaps, the most difficult to guard against, and much of the tediousness of this investigation has arisen from the length of time which it has been necessary to spend in discovering and carrying out, with very small quantities of material, processes of purification suitable to the exceptional character of these alkaloïds.

In the present enquiry, every precaution has been taken to avoid the three important sources of error refered to above.

In a paper communicated to the Society last year by one of us in conjunction with Dr. W. H. Ince (Trans., 1891, **59**), the principal properties of a crystalline alkaloïd derived from carefully selected commercial roots of *Aconitum napellus* were fully described. The alkaloïd had been extracted from the roots by means of a process which avoided all risk of decomposing the natural constituents. Special pains were taken to completely purify the base, and satisfactory evidence was furnished as to its homogeneity. This alkaloïd was evidently the same substance as that first obtained by Wright from commercial roots of *A. napellus*, but in a purer condition. Two of the sources of error alluded to above as vitiating most of the previous work on the subject were thus removed. A third, however, still remained to be dealt with. This alkaloïd had been obtained from carefully selected commercial roots stated to be those of *A. napellus*, but it has been asserted by those botanists who have paid particular attention to this subject, notably by Mr. E. M. Holmes, that it is most difficult, if not impossible, to judge from the appearance of the roots alone whether they belong to the true *A. napellus*. It is necessary, for the purposes of identification, that the flowers and leaves should also be examined. On account of this doubt as to the authenticity of the roots from which this specimen of alkaloïd had been obtained, we considered it desirable to ascertain whether this same alkaloïd is present in the genuine *A. napellus*. We also wished to settle the question as to whether other alkaloïds accompany it in the plant, for on this point there is at present no trustworthy information.

Fortunately we have had no difficulty in securing a small supply of the roots of the true *A. napellus*. The plants were selected and grown at Sevenoaks by Mr. E. M. Holmes at the instance of the British Pharmaceutical Conference. Their botanical characters have already been described by Mr. Holmes (*Trans. Brit. Pharm. Conf.*, 1888).

Alkaloïdal Constituents of the Juice of the Roots.

As the fresh roots were moist with natural juice, an examination was made of the alkaloïds contained in it, since it appeared interesting to determine to what extent the alkaloïds are present in the juice as soluble salts, and how far they occur in an insoluble form in the cells of the root.

Ten kilos. of the fresh roots were submitted to hydraulic pressure, amounting to $1\frac{1}{2}$ tons to the square inch. By this means, about 4·5 kilos. of liquid were obtained. To complete the removal of the soluble alkaloïdal salts, about 3·5 litres of water were allowed to soak into the pressed roots, which were then again submitted to hydraulic pressure. This operation furnished an additional 3·5 kilos. of liquid. A single drop of the mixed liquid, when placed on the end of the tongue, at once gave rise to the characteristic tingling sensation produced by crystalline aconitine. It was found to be almost impossible to filter the turbid liquid, and, owing to its viscosity, organic solvents (ether, chloroform, &c.), did not readily separate from it in distinct layers.

The greater part of the proteïd was therefore precipitated by the addition of acetic acid, and the filtered solution shaken with chloroform, which removed a small quantity of resin and a little of the alkaloïdal acetates. Excess of sodium hydrogen carbonate was then added to the acid liquid, and the alkaloïd extracted by agitation with chloroform; the chloroform solution, on evaporation, left a gummy, alkaloïdal residue. Since the amount of alkaloïd was small, the remainder of the roots (about 15 kilos.) was dealt with in an exactly similar manner, the juice being obtained by hydraulic pressure.

Examination of the Alkaloïds from the Juice.—The brown resinous mass derived from the solution in chloroform showed no signs of crystallising, even after prolonged standing. Its weight was nearly 13·5 grams, and as about 25 kilos. of fresh roots had been used for its production it follows that the juice contains about 0·05 per cent. of the total alkaloïd present in the roots.

The mass was mixed with ether, and the mixture heated for some hours. About three-fourths of the total alkaloïd dissolved in the ether, nearly one-fourth remaining undissolved even after prolonged digestion. The total alkaloïd was thus divided into two portions, a greater part soluble in ether as well as in chloroform, and a smaller portion soluble in chloroform, but insoluble in ether.

Alkaloïds Soluble in Ether.—The gummy residue left on evaporating the ether was dissolved in water acidified with acetic acid, and the liquid extracted with chloroform, which removed a little resin and also traces of alkaloïd, since acetates of the aconitine alkaloïds are removed to a slight extent by chloroform from their aqueous solutions. Excess of sodium hydrogen carbonate was then added to the liquid, and the alkaloïd extracted by repeated shaking with ether. The ethereal solution was dried with calcium chloride, the greater part of the solvent distilled off, and the residual solution allowed to evaporate spontaneously, when it left a slightly coloured, gummy residue, which could not be crystallised. As an excessively dilute solution of this residue produced tingling of the tongue, it seemed likely that aconitine was present. The alkaloïd was converted into hydrobromide by exact neutralisation with dilute hydrobromic acid, and on slowly evaporating the neutral solution, a syrup was obtained which deposited a few crystals of *aconitine hydrobromide*, but the quantity was too small for analysis. An attempt was now made to separate the portion which did not further crystallise into two parts. Fractional precipitation of an alcoholic solution with ether, and fractional precipitation of the base itself, alike failed to effect any definite separation, and none of the fractions could be crystallised. Neither could the hydrochloride of the alkaloïd be crystallised. The aqueous solution of the hydrochloride gave an abundant precipitate with auric chloride, but the pale-yellow, amorphous aurochloride could not be crystallised either from its solution in chloroform or in alcohol.

These results proved that we were dealing for the most part with an amorphous alkaloïd containing a small quantity of aconitine.

Like aconitine, the amorphous alkaloïd is soluble in ether and chloroform. It forms salts which do not appear to crystallise, and from which we were unable to separate a crystalline aconitine salt, although we had satisfactory evidence that this alkaloïd was present in the substance.

The residual alkaline liquid which on extraction with ether had furnished the mixture of alkaloïds above described was found still to contain alkaloïd, which was removed by shaking with chloroform. The alkaloïd thus extracted resembled that dissolved by ether. Neither the base nor its salts would crystallise. The aurochloride, however, deposited a few crystals from an alcoholic solution when this was slowly evaporated. These melted at 134·25° (corr.). Aconitine aurochloride melts at 135·5°.

Alkaloïd Soluble in Chloroform but not in Ether.—The small quantity of alkaloïd which was dissolved from the alkaline solution by chloroform and was not soluble in ether was converted into hydrobromide, and the solution of this salt concentrated by exposure in a vacuous desiccator; no crystallisation occurred, and attempts to produce crystalline salts were not successful. The base dissolved readily in water and alcohol, less readily in chloroform, and hardly at all in dry ether. Fractional precipitation of a solution in chloroform by ether did not lead to the isolation of a crystalline product. Although the base was nearly insoluble in dry ether, yet it may be partly removed from an alkaline solution by extraction with ether, especially in presence of the alkaloïd above referred to as soluble in ether. This peculiarity accounts for the fact that some of this base was also found in the ether-soluble alkaloïd obtained as above described.

This amorphous alkaloïd resembled aconine in its properties, but the quantity obtained was insufficient for analysis.

The juice expressed from the roots, therefore, contains (1) a considerable quantity of amorphous alkaloïd or alkaloïds, soluble in ether; (2) a smaller quantity of an alkaloïd, probably identical with aconitine; (3) a small amount of an amorphous alkaloïd insoluble in ether, probably identical with aconine.

The greater part of the alkaloïds had evidently remained in the roots, and has not been expressed with the juice.

Alkaloïdal Constituents of the Pressed Roots.

The almost dry mass from which the juice had been expressed was now examined. It may be concluded that all the alkaloïdal salts soluble in water had been removed from it by the previous operation.

The pressed roots were dried at about 50°, finely powdered, and the alkaloïdal salts removed by percolation with steam-distilled fusel oil (b. p. 100—132°). The pale-yellow solution was shaken several times with water containing 1 per cent. of sulphuric acid,* and the aqueous layer removed. Dissolved amyl alcohol was now extracted by shaking the acid liquid with chloroform, which also removed resin. Dilute ammonia was then added in very slight excess, and the solution extracted several times with ether. The ethereal solution of the alkaloïd was dried with calcium chloride, the ether partly removed by distillation, and the remainder spontaneously evaporated.

The alkaline liquid from which the alkaloïd soluble in ether had been removed was repeatedly extracted with chloroform, and the chloroform distilled off, when a resinous alkaloïdal residue remained.

Alkaloïd Soluble in Ether.—The residue from the ethereal solution was a slightly coloured gummy mass, which did not crystallise after prolonged standing. It was therefore converted into the hydrobromide by dissolution in very dilute hydrobromic acid, and the exactly neutral solution slowly evaporated† in a desiccator. By this means a crystalline hydrobromide was obtained, which, after recrystallisation and drying, melted at 163° (corr.). From this salt, which corresponded in its properties with aconitine hydrobromide, the alkaloïd was regenerated by adding a slight excess of dilute ammonia to an aqueous solution, and extracting the base with ether. The dry ethereal solution, when spontaneously evaporated, deposited crystals, which melted at 188·6° (corr.), which has been shown in Part I of this investigation to be the melting point of pure aconitine. The aurochloride was prepared by precipitation in the usual manner, and subsequently crystallised from alcohol. When dry, it melted at 135·5° (corr.), the melting point of aconitine aurochloride.

In order to completely establish the identity of the alkaloïd with aconitine, the aurochloride was burned. The following results were obtained:—

Weight of aurochloride, 0·155 gram; weight of carbon dioxide obtained, 0·2278 gram; weight of water obtained, 0·068 gram.

	Found.	Calculated for $C_{33}H_{45}NO_{11},HAuCl_4$.
C	40·08 per cent.	40·12 per cent.
H	4·87 ,,	4·66 ,,
Au	19·7 ,,	19·99 ,,

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* Very dilute sulphuric acid was employed instead of an organic acid, because sulphuric acid of this strength had been found not to hydrolyse aconitine under the conditions of the experiment, whilst some organic salts of aconitine occasion trouble by passing out of the acid liquid when it is shaken with chloroform.

† Aconitine is readily hydrolysed if evaporated in a solution acid with hydrobromic acid, but a neutral solution of the hydrobromide may be heated at 100° without decomposition.

These results prove the alkaloïd to be aconitine, and incidentally furnish confirmatory evidence of the correctness of the formula $C_{33}H_{45}NO_{11}$, proposed for aconitine in Part I.

In the previous paper, it was shown that this alkaloïd is remarkable in forming salts which are lævorotatory, although solutions of the alkaloïd itself are dextrorotatory. The specific rotation of the hydrobromide now obtained was determined, with the following result:—

$\alpha[20°] = -1·1625°$ (mean of four determinations); $l = 2$ dm.; $d\ 20/20° = 1·0053$; $p = 1·95$;

whence, $$[\alpha]_D = \frac{100 \times 1·1625}{2 \times 1·95 \times 1·0053} = -29·65.$$

This number agrees with that previously recorded in Part I, namely, $[\alpha]_D = -30·47°$.

Having thus obtained a small supply of pure aconitine, the opportunity was taken of ascertaining the solubility of the alkaloïd in water. As mentioned in the previous paper (Part I), Jürgens had recorded it as 1 gram in 726·4 grams of water at 22°, but we had observed that the pure alkaloïd was far less soluble than this. A weighed quantity of aconitine was finely powdered, and digested with water at 22° during two days. A known quantity of the solution was evaporated to dryness, and the residue of aconitine weighed. The following results were obtained:—

I. 72·488 grams of solution yielded 0·0164 gram of aconitine. Hence 1 gram of aconitine dissolves in 4420 grams of water.
II. 150·15 grams of solution yielded 0·0338 gram of aconitine. Hence 1 gram of aconitine dissolves in 4442 grams of water.

The mean result of these two determinations is 1 in 4431, which may be taken as the solubility of aconitine in water at 22°.

Napelline.—The syrupy liquid from which all the aconitine hydrobromide had crystallised, after prolonged standing in a desiccator, was reconverted into alkaloïd by the addition of a slight excess of ammonia to its aqueous solution. Ether extracted from this liquid an alkaloïd, which, on evaporation of the ether, remained as a pale-yellow mass resembling a gum. It was almost entirely soluble in anhydrous ether. The ethereal solution, when evaporated, left a resinous mass, which could not be crystallised; when quite dry, it was easily powdered. The base dissolved only sparingly in water, but the aqueous solution was alkaline and extremely bitter; unlike aconitine, it produced no tingling sensation. The alkaloïd is readily soluble in alcohol and ether, less readily in chloroform, and scarcely at all in light petroleum. Its solutions are lævorotatory.

The base dissolves in dilute acids forming salts which are left as varnishes on the evaporation of the solvent. Many unsuccessful attempts were made to crystallise the hydrobromide, hydrochloride, and nitrate both from alcoholic and from aqueous solutions. Alkalis precipitate the base from solutions of its salts in white flocks.

On the addition of auric chloride to an aqueous solution of the hydrochloride, a pale-yellow, amorphous aurochloride is precipitated. This, when dry, melted somewhat indefinitely near 110°. It could not be crystallised from its solution in alcohol or chloroform.

The properties of this alkaloïd are being more fully investigated. It is evidently the substance which has been observed to cling obstinately to crystalline aconitine, and which appears as a "gummy ring" when solutions of impure aconitine are evaporated. The two alkaloïds may, however, be almost completely separated by conversion into the hydrobromide, when the crystalline hydrobromide of aconitine may be removed from the syrupy residue of the uncrystalline hydrobromide of the new base. Since we were unable to obtain a crystalline compound or derivative of the substance, it was not possible to ascertain with certainty whether it was free from other impurity than aconitine; the last traces of the latter alkaloïd are not easy to remove.

The facts above recorded prove that this amorphous base occurs naturally in *Aconitum napellus*, and that it is not a decomposition product of aconitine. Its properties do not correspond with those of the amorphous bases obtained by previous workers. It is distinguished from the picraconitine of Wright by not readily forming crystalline salts. It differs from aconine by its solubility in ether, and sparing solubility in water. We propose to revive for it the name *napelline*, which, although twice proposed for alkaloïdal products derived from aconite roots, has never been widely used and is now no longer applicable to any single alkaloïd. Its great advantages as a designation for a second alkaloïd of *Aconitum napellus* are obvious. The name napelline was first applied by Wiggers to the alkaloïd now known as pseudaconitine, and afterwards Hübschmann used it as a name for an alkaloïd he extracted from *Aconitum napellus*, which the experiments of Wright showed to be a mixture chiefly composed of aconine, resulting from the decomposition of aconitine during its extraction from the root. The alkaloïd, which we suggest should be called napelline, was observed to be present in the roots of *A. napellus*, to quite as large an extent as aconitine.

Considerable progress in the tedious work of purifying and characterising this alkaloïd has since been made by one of us in conjunction with Mr. E. F. Harrison. The preparation of a crystalline compound of napelline has made it possible to obtain the alkaloïd in an unquestionably pure state, but the operation is one of the most tedious and laborious that we have yet encountered in this troublesome inquiry. The pure alkaloïd having been at last isolated, its physiological action is being examined. When separated from aconitine in the manner above described, napelline is still contaminated with another alkaloïd, which does not crystallise or furnish crystalline salts. On account of its resemblance to napelline, we propose to call this substance *homo-napelline.*

Alkaloïd Insoluble in Ether but Soluble in Chloroform.—The alkaline solution from which the alkaloïd soluble in ether had been removed, was shaken with chloroform. This dissolved a resinous substance, which afforded alkaloïdal reactions. The mass was washed with water, which dissolved the greater part, leaving a little resin undissolved. By extracting the aqueous solution with chloroform, the alkaloïd was removed, and remained after evaporation of the solvent, as an amorphous residue. This was found to be nearly but not quite insoluble in dry ether, a small quantity of napelline being dissolved. In order to completely remove napelline, the alkaloïd was dissolved in chloroform, and the solution precipitated with anhydrous ether. By several repetitions of this process, a colourless, deliquescent resin was obtained, entirely soluble in cold water and in alcohol, but scarcely soluble in dry ether or light petroleum. Numerous attempts were made to crystallise the base, but without success. In all these respects this alkaloïd corresponds with aconine, the basic hydrolytic product of aconitine, some of whose properties were described in Part I, and are now more fully elucidated in Part III, which follows this paper. The dry base was analysed with the following results:—

Weight of substance, 0·1078 gram; weight of carbon dioxide, 0·2258 gram; weight of water, 0·0776 gram.

	Found.	Calculated for $C_{26}H_{41}NO_{11}$.
C	57·12	57·44 per cent.
H	7·99	7·73 „

The base is thus proved to be *aconine.* There can be no doubt that this alkaloïd actually exists in the roots of *A. napellus*, since the process used in its isolation is such that it could not have been formed by the hydrolysis of aconitine. The amount of aconine contained in the roots is very slightly if at all less than that of aconitine.

The precise relationship of aconine to aconitine has not hitherto been satisfactorily established. Its properties have suggested that it may not, perhaps, stand in the simple relation to aconitine which the equation representing its formation by hydrolysis would imply, $C_{33}H_{45}NO_{11} + H_2O = C_7H_6O_2 + C_{26}H_{41}NO_{11}$. Isomeric change or molecular condensation may have accompanied hydrolysis. In order to ascertain whether aconine is a polymeride of the formula $(C_{26}H_{41}NO_{11})_n$, the molecular weight of the base was determined by Raoult's method, acetic acid being used as the solvent. The following are the experimental data:—

Weight of substance..........	0·116 gram
Weight of solvent............	6·1402 grams
Freezing point of solvent......	14·973°
„ solution	14·833°
Depression for 1 gram of substance to 100 grams of solvent	0·0741°
Mol. depression of acetic acid ..	39

Hence molecular weight of aconine = 526; molecular weight calculated from formula $C_{26}H_{41}NO_{11}$ = 543.

This result is remarkably near that calculated for the formula $C_{26}H_{41}NO_{11}$, when it is remembered that a difference of 0·01° in the reading of the thermometer corresponds with a difference of about 40 in the molecular weight, and that no correction has been made for the formation of aconine acetate. The connection between aconine and aconitine has been placed beyond question by the experiments to be described in Part III.

This inquiry has proved that the roots of true *A. napellus* contain four alkaloïds. Only one of these has so far been crystallised, namely, aconitine, whose chief physical and chemical properties, and those of its characteristic compounds, have been described in Part I (Trans., 1891). The quantity of the three uncrystalline alkaloïds *aconine*, *napelline*, and *homo-napelline* occurring in the roots is more than twice as great as that of aconitine. The properties of napelline and homonapelline are now being further investigated.

The physiological action of these four alkaloïds derived from *A. napellus* is being examined. The results so far obtained prove that aconitine is by far the most poisonous of them, and, indeed, it appears to be the most toxic of the vegetable alkaloïds.

XXXIII.—COMMUNICATIONS FROM THE RESEARCH LABORATORY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

Contributions to our Knowledge of the Aconite Alkaloïds. Part III. *The Formation and Properties of Aconine and its Conversion into Aconitine.*

By WYNDHAM R. DUNSTAN, M.A., and F. W. PASSMORE, Ph.D.

IN a previous paper (Part I, Trans., 1891, **59**, 271), one of us, in conjunction with Dr. W. H. Ince, has described the principal properties of crystalline aconitine derived from *Aconitum napellus.* The differences between the chemical properties of the alkaloïd described by us and those recorded by previous workers prove that the substance we obtained was purer than any specimen hitherto described. Experiments then recorded showed that, on hydrolysis, aconitine breaks up, apparently, in accordance with the equation $C_{33}H_{45}NO_{12} + H_2O = C_{26}H_{41}NO_{11} + C_7H_6O_2$, benzoic acid being formed, together with an amorphous base, first obtained by Wright and Luff, and named by them aconine. Much uncertainty, however, still exists with reference to the mode of formation and properties of this alkaloïd, and since these points are of fundamental importance in connection with the question as to the constitution of aconitine, we determined to investigate the nature of the base or bases resulting from the hydrolysis of the pure alkaloïd. Wright and Luff (Trans., 1878, **33**, 318) assert that aconine results from the action of water at a high temperature, or of a mineral acid, or of alkalis on aconitine, the change occurring in accordance with the equation given above. They describe the base as being a slightly-coloured, friable, hygroscopic mass, readily soluble in water and alcohol, but nearly insoluble in ether. The aqueous solution is stated to be bitter, but to produce no tingling sensation. It melts near 130°, and its composition is represented by the formula $C_{26}H_{39}NO_{11}$. Neither the base nor its salts could be crystallised. Wright and Luff further state that aconine acts as a reducing agent on salts of gold and silver. The products of the hydrolysis of aconitine point to the conclusion that this alkaloïd is benzoylaconine, and although Wright and Luff failed to reconvert aconine into aconitine by heating it with benzoic anhydride, they obtained what was probably benzoylapoaconitine.

Dragendorff and Jürgens* (*J. Pharm.* [3], **18**, 277) have questioned the accuracy of the account of the hydrolysis of aconitine given by Wright and Luff. They assert that the hydrolysis occurs in two stages. In the first stage one molecular proportion of benzoic acid is separated with formation of a base which they state is identical with the picraconitine found by Wright and Luff in one commercial sample of roots, reputed to be those of *A. napellus*. In the second stage, picraconitine undergoes hydrolysis, losing a molecular proportion of benzoic acid, together with methyl alcohol, and furnishing aconine, which is the final product of the change. If these facts are correct, aconitine must be regarded as dibenzoylmethoxyaconine.

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* We have not been able to refer to the original paper, and are therefore

Hydrolysis of Aconitine.

The main purpose of our experiments was to ascertain whether any base, other than aconine, can be found at any stage of the hydrolysis of aconitine.

Pure aconitine (m. p. 188·5°, corr.) was heated for several hours with water in a closed tube at 150°. Water was used in preference to alkali or acid, so that the change might take place gradually, and without the resinification which always results from the use of alkali. The details of an experiment are as follows:—1 gram of aconitine was heated with 25 c.c. of water in a closed tube at 150—155° for 10 hours. After this treatment, the liquid still produced the tingling sensation characteristic of aconitine, and, therefore, presumably the whole of the latter had not suffered decomposition. On distillation, the liquid afforded no methyl alcohol or other volatile product. The solution was acidified with dilute sulphuric acid and extracted with ether, until nothing further was removed. The ethereal solution was washed, dried, and distilled; the residue of benzoic acid weighed nearly 0·1 gram, that is, about 10 per cent. of the aconitine taken; the quantity of benzoic acid calculated from the equation given above is 18·8 per cent.; rather more than one-half of the aconitine had, therefore, undergone hydrolysis, if the equation is correct. The acid solution from which the benzoic acid had been removed was made alkaline with ammonia, and completely extracted with ether. The ethereal solution left, on evaporation, an amorphous residue, weighing 0·35 gram. This residue gave rise to the tingling sensation. Its properties suggested that it was a mixture of aconine and aconitine, and it was found that although dry aconine is insoluble in anhydrous ether, it may be extracted to some extent by ether from an aqueous solution, especially when aconitine is also present.

The liquid which had been extracted with ether was now shaken

obliged to depend upon the abstract in English, which gives no experimental details.

with chloroform, which removed aconine with a trace of resin; the residue left on evaporating the chloroform solution weighed 0·2 gram.

Excess of baryta-water was now added to the alkaline solution, which was evaporated to expel ammonia, and filtered from barium sulphate; the excess of baryta was then precipitated by the requisite quantity of dilute sulphuric acid. The filtrate, when evaporated to dryness, left a residue weighing 0·43 gram, which was almost entirely soluble in alcohol, and consisted of nearly pure aconine. The residues from the solutions in ether and chloroform were found to be mixtures of aconitine and aconine, and on heating them with water in a closed tube as before, more benzoic acid was formed, and substances soluble in ether, chloroform, and water were again obtained. The tingling sensation produced by the original liquid proved that aconitine was still present. By a repetition of this process, nearly the whole of the original alkaloïd was converted into aconine. No methyl alcohol was found at any stage in the process, and no trace of an alkaloïd having the properties of picraconitine could be detected.

The hydrolysis of aconitine was then repeated in the manner above described with several quantities of aconitine, varying from 1 to 5 grams, in every instance, with the same result: only benzoic acid and aconine were formed and neither methyl alcohol nor picraconitine could be isolated. We are, therefore, justified in concluding that the hydrolysis of aconitine into aconine and benzoic acid takes place in accordance with the equation given above.

The amorphous base, not aconine, which Dragendorff and Jürgens thought to be picraconitine, may have been napelline, arising from impure aconitine having been employed. The circumstance that aconine, though insoluble in ether when dry, is nevertheless extracted from aqueous solution both by ether and chloroform, especially when aconitine and napelline are present, may also have led to the conclusion that some alkaloïd other than aconine had been formed. We regard it as probable that the methyl alcohol, supposed by these observers to be formed during the hydrolysis of aconitine, also took its origin in the use of impure aconitine, since we have noticed that organic solvents obstinately cling to the imperfectly crystallised alkaloïd and are set free when it is boiled with water. No such effect is observed when pure aconitine is employed.

Properties of Crystalline Aconine Hydrochloride.

Up to the present time, aconine has been described as an amorphous base, which forms amorphous salts. Wright and Luff speak of it as an amorphous, resinous alkaloïd (m. p. 130°), readily soluble in water and alcohol, soluble also in chloroform, but insoluble in ether. Its aqueous solution reduces salts of gold and silver, and also Fehling's solution. The salts formed from it were amorphous, and were not obtained pure.

In the course of the experiments relating to the hydrolysis of pure aconitine, a few grams of aconine were obtained. With this material we have studied the properties of the alkaloïd. This specimen of aconine was purer than any we had previously obtained, being almost if not entirely free from the resin which is formed along with it when aconitine is acted on by alkalis. Its aqueous and alcoholic solutions did not crystallise when slowly evaporated in a desiccator, but finally dried up to a nearly colourless, friable, resinoid mass. The aqueous solution was decidedly alkaline, and had powerful reducing properties. Its taste was slightly bitter, but the tingling sensation produced by aconitine was quite absent.

Since the base could not be crystallised, an attempt was made to crystallise its salts. The aqueous solution was exactly neutralised with dilute hydrochloric acid, and evaporated to a very small volume on the water-bath. The syrupy liquid, which at first showed no signs of crystallising, was allowed to stand for several days in a vacuous desiccator over calcium chloride. It slowly became crystalline. The minute crystals were white, but the syrup which surrounded them was slightly coloured. The mixture was, therefore, drained on a porous tile in a desiccator, by which means the crystals were separated almost entirely from the coloured syrup. This plan of purification was found to be less wasteful and more effective than recrystallisation from water or alcohol; the salt absorbed by the tile was washed out, and more crystals were obtained from the solution. The white, dry mass removed from the tile consisted of minute crystals. Before their properties were examined, they were recrystallised by the addition of ether to an alcoholic solution. The crystals were dissolved in a small quantity of strong alcohol and anhydrous ether was then added until a faint turbidity appeared; on standing in a stoppered bottle, this solution deposited colourless rosettes of needle-shaped crystals, a further quantity being obtained by the addition of more ether to the remaining liquid.

When dried at 100°, these crystals of aconine hydrochloride lost water without darkening; 0·25025 gram of salt lost 0·0077 gram of water at 100°; that is, 2·92 per cent. When the temperature was raised to 120°, and the heating continued for a few hours, there was a further loss of 0·0158 gram, after which the weight of the salt remained constant. The total loss in weight amounted, therefore, to 6·31 per cent.

It appears from these results that the crystalline hydrochloride contains two molecular proportions of water, and is represented by the formula $C_{26}H_{41}NO_{11},HCl,2H_2O$. One molecular proportion of the water is lost at 100° and the other at 120°; thus:—

	Loss calculated from the formula $C_{26}H_{41}NO_{11},HCl,2H_2O$.	Found.
$1H_2O$........	3·08 per cent.	2·92 per cent.
$2H_2O$........	5·95 ,,	6·31 ,,

The dry salt is very hygroscopic and when exposed to air gradually absorbs the equivalent of one molecular proportion of water. In order to confirm the accuracy of the formula given above, the amount of chlorine in the dried hydrochloride was determined with the following results:—

I. 0·1550 gram of salt gave 0·037 gram of silver chloride; 5·93 per cent.
II. 0·3920 gram of salt gave 0·0975 gram of silver chloride; 6·15 per cent.
III. 0·3678 gram of salt gave 0·0917 gram of silver chloride; 6·22 per cent.

The mean of these three determinations of the chlorine is 6·13 per cent., whilst the amount calculated from the formula $C_{26}H_{41}NO_{11},HCl$ is also 6·13 per cent.

Anhydrous aconine hydrochloride melts at 175·5° (corr.). It readily dissolves in water and alcohol, and is slightly soluble in chloroform, but is nearly insoluble in ether and light petroleum. The aqueous solution has at first a bitter-sweet and afterwards a burning taste. Like aconitine hydrochloride, it exerts a lævorotatory action on polarised light, but its effect is much feebler. The anhydrous salt was employed in determining the specific rotation of an aqueous solution with the following result:—

$$\alpha[15^\circ] = 0{\cdot}9^\circ;\ l = 2\text{ dm.};\ p = 5{\cdot}75;\ d\ 15^\circ/4^\circ = 1{\cdot}015,$$

whence
$$[\alpha]_D = \frac{100 \times -0{\cdot}9}{2 \times 1{\cdot}015 \times 5{\cdot}75} = -7{\cdot}71^\circ.$$

The aqueous solution of aconine hydrochloride is neutral to litmus and is not precipitated by alkalis even when concentrated. Picric acid does not precipitate the solution, neither does gold chloride, except in strong solutions, when an amorphous, pale-yellow precipitate is produced.

Other Crystalline Salts of Aconine.

Besides the hydrochloride, the *hydriodide*, *hydrobromide*, and *sulphate* were crystallised. All these salts are very soluble in water, and do not crystallise as readily as the hydrochloride. The crystalline sulphate is especially difficult to obtain; the aqueous solution when exposed in a desiccator, evaporates to a thick syrup without crystallising. On standing, very fine needle-shaped crystals appear in the viscous liquid, and are most difficult to separate from it.

Properties of Pure Aconine.

Aconine was prepared from the pure hydrochloride by adding silver sulphate to the aqueous solution, slightly more silver salt being added than was required to precipitate the chloride. The precipitate of silver chloride was filtered off and the small excess of silver sulphate removed as sulphide. The solution of aconine sulphate thus obtained was precipitated by the addition of exactly the requisite quantity of baryta-water, the barium sulphate filtered off, and the filtrate evaporated to a small volume on the water-bath. The syrupy liquid was exposed in a desiccator, when it slowly dried up, without crystallising, to a colourless, hygroscopic, gum-like mass, which could not be crystallised from any of its solutions.

The amorphous base melts at 132° (corr.) without decomposition. On combustion, it afforded the following data:—

I. Weight of base, 0·1245 gram; weight of carbon dioxide, 0·2614 gram; weight of water, 0·08985 gram.

II. Weight of base, 0·30610 gram; weight of carbon dioxide, 0·6437 gram; weight of water, 0·22105 gram.

	I.	II.	Calculated for $C_{26}H_{41}NO_{11}$.
C	57·27	57·35	57·46
H	8·02	8·02	7·55

The fact that the hydrogen is rather higher than the calculated quantity is to be accounted for by the extremely hygroscopic character of the base, which makes it difficult to manipulate without absorption of water.

Aconine is very soluble in water or alcohol, and slightly in chloroform, but insoluble in ether and light petroleum. The aqueous solution reduces salts of gold and silver and also Fehling's solution. It is precipitated by the general alkaloïdal reagents, and mercuric chloride produces a copious yellowish-white precipitate, which darkens on standing.

The aqueous solution is decidedly alkaline and dextrorotatory. The determination of the specific rotation afforded the following results:—

$$\alpha[15] = +1·65;\ l = 2\text{ dm.};\ p = 3·534;\ d\,15°/4° = 1·01,$$

whence $$[\alpha]_D = \frac{100 \times 1{\cdot}65}{2 \times 3{\cdot}534 \times 1{\cdot}01} = +23^\circ.$$

Aconine thus possesses the same peculiarity as was shown in Part I of this paper to belong to aconitine, the base being dextrorotatory and the salts lævorotatory.

When boiled with alkalis, aconine darkens and slowly resinifies. The physiological action of aconine is being investigated; it does not appear to be poisonous in small doses.

Formation of Benzoylaconine. Conversion of Aconine into Aconitine.

The question as to the exact relationship of aconine to aconitine has been to a certain extent elucidated by the experiments already described. It has been shown that pure aconitine yields only aconine and benzoic acid when hydrolysed and that the molecular formula of aconine is $C_{26}H_{41}NO_{11}$. It is, therefore, almost certain that aconitine is benzoylaconine. If this conclusion is correct, it should be possible to prepare aconitine from aconine by introducing a benzoyl group. By the action of benzoic anhydride on aconine, Wright and Luff obtained, not aconitine, but a base probably identical with benzoylapoaconitine which did not, apparently, exert the characteristic physiological action of aconitine. We have repeated this experiment with pure aconine, which was heated with benzoic anhydride in a closed tube at 100—130° for about three hours. No aconitine could be detected in the product. Some aconine was recovered unchanged, together with an amorphous base, which did not give rise to the tingling sensation and was not further examined. It appears to be the same substance as that isolated by Wright and Luff.

Since aconitine is so readily hydrolysed by acids and alkalis, we did not attempt to introduce the benzoyl group by means of benzoyl chloride and alkali after the manner proposed by Baumann and Udransky.

The strongly basic properties of aconine suggested the probability that it might be able to decompose ethyl benzoate with the formation of ethyl alcohol and aconitine, or if the temperature of reaction were high enough to cause dehydration of the aconitine, anhydro-aconitine might be the final product. The reaction may be expressed by the equations

$$\text{(i.)}\quad C_6H_5{\cdot}COOEt + C_{26}H_{41}NO_{11} = EtOH + \underset{\text{(Aconitine).}}{C_{26}H_{40}(C_6H_5{\cdot}CO)NO_{11}.}$$

$$\text{(ii.)}\quad \underset{\text{(Aconitine.)}}{C_{33}H_{45}NO_{12}} = H_2O + \underset{\text{(Anhydro-aconitine).}}{C_{33}H_{43}NO_{10}.}$$

It was found that aconine did not readily react with ethyl benzoate under ordinary pressure, and the experiment was therefore made in a closed tube.

Half a gram of pure aconine was dissolved in 10 c.c. of alcohol, and 0·2 gram of ethyl benzoate added to the mixture, which was heated in a closed tube at 130° for three hours. Some ethyl benzoate remained unattacked at the close of the experiment. The liquid was heated in an open flask on the water-bath until all the alcohol had evaporated. Water was then added and the liquid acidified with dilute hydrochloric acid; a drop of this solution produced the characteristic tingling sensation on the tongue. Unaltered ethyl benzoate and benzoic acid were now removed by extracting the liquid with ether, the solution was rendered alkaline with dilute ammonia, and the alkaloïd extracted with ether. The ethereal solution, on evaporation, left a resinoïd mass which did not crystallise. By neutralisation with dilute hydrobromic acid and evaporation of the solution, a colourless, crystalline hydrobromide was obtained. From this salt the alkaloïd was regenerated, dissolved in dilute hydrochloric acid, the solution precipitated with gold chloride, and the pale-yellow precipitate of aurochloride washed and dissolved in alcohol. By the gradual addition of water to the alcoholic solution, the salt was deposited in crystals which melted at 141° (corr.). The aurochloride of anhydro-aconitine melts at exactly this temperature (Part I).

By the reaction of aconine with ethyl benzoate, we had thus obtained the anhydride of aconitine, and since this compound may be converted into aconitine, a partial synthesis of the natural alkaloïd has been effected, and the relationship of aconine and aconitine demonstrated beyond question.

It is intended to make further experiments on the conversion of aconine into aconitine and also to prepare other compounds of aconine containing various acid radicles. The examination of the physiological action of these aconine derivatives is likely to throw light on the cause of the intensely toxic property with which the non-poisonous aconine becomes endowed when a benzoyl group is grafted on to its molecule.

Decomposition Products of Aconine.

The behaviour of aconine when attacked by various reagents has been closely investigated, but so far without much success, as it has not been possible to crystallise the principal decomposition products.

Nitrous acid does not appear to react with aconine. 0·7 gram of pure aconine was dissolved in 5 c.c. of water and mixed with a solution of 0·1 gram of sodium nitrite in 20 c.c. of water. The requisite quantity of dilute hydrochloric acid was then gradually added to the well-cooled mixture. After standing for some time, until the evolution of nitrous fumes had ceased, the solution was made alkaline and extracted with ether, which, however, removed nothing appreciable. The aqueous solution was exactly neutralised with dilute hydrochloric acid and evaporated to dryness; the residue extracted with boiling alcohol, and the solid left on the evaporation of the solvent again extracted with cold alcohol. Neither of these solutions contained any substance giving Liebermann's reaction for a nitroso-derivative and after evaporation in a desiccator and long standing, the latter solution furnished crystals of aconine hydrochloride.

The *oxidation* of aconine was effected with potassium permanganate in the following manner. About 1 gram of aconine dissolved in water was oxidised by the gradual addition of 3 grams of potassium permanganate, solution of potassium carbonate being added from time to time so that the liquid was always alkaline. The mixture was heated on the water-bath to complete the oxidation, then cooled and filtered. The precipitate of manganese oxide was extracted with alcohol, which removed a little resin. The filtrate was acidified with hydrochloric acid and extracted with ether, which removed very little. After it had been rendered alkaline with ammonia, the solution was extracted with chloroform and subsequently with ether but nothing appreciable was dissolved from the aqueous solution by either solvent. The solution was now evaporated to a small volume on the water-bath and precipitated with lead nitrate. The precipitate, which contained some lead chloride, was collected, washed, and decomposed with hydrogen sulphide. The filtrate from the lead sulphide, when evaporated, deposited crystals of oxalic acid; these were converted into the silver salt, which was analysed. It contained 71·24 per cent. of silver; silver oxalate contains 71·05 per cent.

The filtrate from the precipitate produced by lead nitrate was evaporated, and the lead removed by hydrogen sulphide. No crystalline acid or other product could be obtained from the solution.

Action of Methyl Iodide on Aconine and Aconitine. Formation of Aconitine Methiodide and Methhydroxide.

The action of methyl iodide on aconine and on aconitine has been studied under various conditions. So far, no crystalline additive compound has been obtained from aconine, although it appears that when this alkaloïd is heated with methyl iodide for several hours in a closed tube at 100°, a base is formed which neither crystallises itself nor yields crystalline salts. This substance has not yet been further examined.

A crystalline additive compound of aconitine with methyl iodide is readily obtained.

Half a gram of pure aconitine was dissolved in a considerable excess of methyl iodide. On heating the mixture at 100° in a closed tube, nearly colourless crystals soon began to separate, and gradually increased in number until at last the mixture became semi-solid. The excess of methyl iodide was drained from the crystals and found to contain scarcely any of the new compound, which seems to be only slightly soluble in this liquid. The crystals were dissolved in methyl alcohol and crystallised from the solution by the gradual addition of ether. By this means, *aconitine methiodide* was obtained in rosettes of crystals having a faint yellow tint; these, after drying at 100°, melted at 219·5° (corr.). The methiodide dissolves in alcohol, water, and chloroform, less readily in light petroleum and in ether. The aqueous solution is neutral to litmus. On analysis, the methiodide furnished the following result:—

> 0·2567 gram dissolved in 20 c.c. of water and precipitated with a slight excess of silver sulphate gave 0·0762 gram of silver iodide. The salt thus contains 16·04 per cent. of iodine. The formula $C_{33}H_{45}NO_{12},CH_3I$ requires 16·09 per cent.

From the filtrate obtained in this experiment, the silver was removed by hydrogen sulphide, and then the free sulphuric acid was exactly precipitated with baryta-water. This solution of the *sulphate* deposited no crystals when slowly evaporated in a desiccator, and eventually dried up to a varnish.

The sulphate was redissolved in water, the aqueous solution made alkaline with ammonia and several times extracted with ether. The ethereal solution of *aconitine methhydroxide*, $C_{33}H_{45}NO_{12},CH_3{\cdot}OH$, on evaporation furnished a resinous residue which could not be crystallised. The *aurochloride* appears as a pale-yellow, amorphous precipitate when a solution of auric chloride is added to an aqueous solution of the hydrochloride of the base. This salt did not crystallise from its alcoholic solution.

The properties of aconitine methhydroxide and its salts will be further examined, and it is intended to investigate the physiological action of these compounds.

XXXIV.--CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. XXIV. *Chromic Acid.*

By ELEANOR FIELD, Bathurst Student of Newnham College, Cambridge.

IN *Ann. Chim. Phys.* [6], **5**, 568, Moissan gives an account of crystals obtained by dissolving chromium trioxide in water under special conditions, these crystals agreeing in composition with the formula H_2CrO_4. Moissan says: " Pour obtenir des cristaux d'acide chromique hydraté, on met un excès d'acide chromique anhydre, preparé . . . , en présence d'une petite quantité d'eau. La solution est maintenue quelques heures à 90°; on agite de temps en temps, puis on décante dans un flacon et l'on refroidit le liquide à la température de la glace fondante. Il se dépose alors sur les parois du flacon des petits cristaux rouges." The crystals on analysis gave 84·25 per cent. of CrO_3 and 15·75 per cent. of H_2O; the formula H_2CrO_4 requires 84·79 per cent. CrO_3 and 15·2 per cent. H_2O.

Acting on the suggestion of Mr. Pattison Muir, who has helped and advised me throughout, I repeated the above experiment and obtained crystals which were found, on analysis, to contain no water.

Analyses of pure chromium trioxide crystals, and of the crystals deposited from an aqueous solution of this oxide, according to Moissan's directions, were made side by side, with the following results.

I. *Gravimetric Analysis.*

The chromium was precipitated as barium chromate, or as hydrated sesquioxide, after reduction with hydrochloric acid and alcohol, or sulphur dioxide and sulphuric acid.

Pure trioxide crystals....	100·91	per cent.	CrO_3.
	100·30	,,	,,
	101·10	,,	,,
Crystals deposited from an aqueous solution of the trioxide prepared according to Moissan's directions	100·08	per cent.	CrO_3.
	100·13	,,	,,
	100·90	,,	,,

That the numbers are slightly too high can be accounted for by the extreme instability of chromium trioxide, and its tendency to be reduced to the sesquioxide.

II. *Volumetric Analysis.*

A determinate weight of chromium trioxide was added to a measured volume of a solution of ferrous sulphate of known strength, and the quantity of iron remaining unoxidised was determined by titration with standard permanganate solution; the difference gave the amount of iron oxidised by the chromic acid present. Solutions of the two sets of crystals simultaneously titrated gave the following results:—

Pure trioxide crystals....	99·82 per cent. CrO_3. 100·10 ” ”
Crystals deposited from an aqueous solution of the trioxide	99·0 per cent. CrO_3. 99·23 ” ”

It is somewhat difficult to make sure of the end of the reaction, as the green colour of the chromic sulphate modifies the pink of the permanganate. To obviate this difficulty very dilute solutions were used, and the colour obtained at the end of the reaction was compared with that produced by adding one drop of permanganate to a dilute solution of chromic sulphate.

The crystals of chromium trioxide used were made according to Zettnow's method (*Ann. Phys. Chem.*, **143**, 468). The crystals formed on treating a concentrated aqueous solution of potassium dichromate with concentrated sulphuric acid were spread out on a porous plate for about 24 hours, and then washed with pure nitric acid (sp. gr. 1·46) until they ceased to give the reactions for sulphuric acid and potassium; they were then heated to about 60—80° until fumes of nitric acid were no longer evolved.

The second set of crystals was obtained from a solution of chromic trioxide, prepared according to Moissan's directions:—An almost saturated aqueous solution of the trioxide was heated for about 10 hours to 80—90°, and then placed in a freezing mixture; after a time, small, hard masses of metallic-looking crystals separated.

A portion of the same saturated solution heated for the same length of time in a sealed tube, and then placed in a freezing mixture, gave no crystals; whereas, when the solution was placed in a vacuum over sulphuric acid, crystals were obtained which were similar in appearance to those formed by the first method, and gave the same percentage composition on analysis.

The results of the analyses given above show that the numbers obtained for the crystals deposited from an aqueous solution of chromium trioxide are practically identical with those obtained for the crystals of the trioxide.

In order further to compare the two sets of crystals, a series of experiments was made with Beckmann's apparatus for determining the raising of the boiling point of a solvent by the solution therein of a definite quantity of a substance (*Zeit. physikal. Chem.*, **6**, 437).

The following data show the increases produced in the boiling point of water by definite weights of chromium trioxide, and of crystals deposited from an aqueous solution of this compound, dissolved in specified weights of water:—

	Grams.	Grams water.	Rise of temperature.
I. Chromium trioxide ..	0·8525	30·5	0·185°
	2·0320	40·0	0·420
	0·4910	,,	0·110
	0·9670	,,	0·220
	2·9990	,,	0·640
II. Crystals deposited from an aqueous solution of chromium trioxide	0·334	30	0·075°
	0·443	,,	0·120
	0·5005	,,	0·115
	1·0990	,,	0·180

The effects produced on the boiling point of water by dissolving the two sets of crystals therein are most apparent if the increases are expressed for 2 grams of the substance in each case.

Rise produced by dissolving 2 grams of chromium trioxide in 40 grams of water	0·43°
	0·413
	0·440
	0·450
	0·430

Rise produced by dissolving 2 grams of crystals from an aqueous solution of chromium trioxide in 30 grams of water	0·449°
	0·540
	0·450
	0·330

The crystals are the same in both cases.

It is evident then that when an almost saturated aqueous solution of chromium trioxide has been heated for several hours at a temperature of 80—90°, and then cooled below 0°, it deposits crystals of CrO_3, and not of chromic acid, H_2CrO_4, as stated by Moissan (*loc. cit.*).

But an aqueous solution of chromium trioxide may contain chromic acid, or, perhaps, dichromic acid (? $2CrO_3 + H_2O + Aq = H_2Cr_2O_7,Aq$).

Now it is possible to calculate the molecular weight of a substance in solution from determinations of the decrease in the vapour pressure of the solvent produced by definite weights of the dissolved substance. The foregoing numbers give data for this calculation.

The molecular weights of the substance in an aqueous solution of chromium trioxide, calculated from the data given above, are:— I, 57·1; II, 57·6; III, 60·7; IV, 56·0; V, 55·02. The molecular weight of CrO_3 is 100·4; of H_2CrO_4, 118·4; and of $H_2Cr_2O_7$, 218·8.

It would seem then that the solution examined did not contain any one of these compounds. Ostwald (*Zeit. physikal. Chem.*, **3**, 79) determined the decrease in the freezing point of water produced by dissolving therein a determinate weight of CrO_3; from his results he concluded that the solution contained dichromic acid, $H_2Cr_2O_7$, wholly or almost wholly, dissociated into three ions.

If it is assumed that an aqueous solution of CrO_3 contains a compound dissociated into three ions, the molecular weight of this compound may be found by multiplying the numbers given above by 3. The results of doing this are as follows:—(1) 171·3; (2) 172·8; (3) 182·1; (4) 168·0; (5) 165·06. The mean of these is 171·85, a number which does not agree with the molecular weight of H_2CrO_4 (118·4), nor with that of $H_2Cr_2O_7$ (218·8).

The conclusion which I draw from these results is that, although a solution of chromium trioxide in water deposits the oxide uncombined with water, on cooling, nevertheless this solution does not contain CrO_3 as such, but that a compound of this oxide with water is formed, or, more likely, that compounds are formed, probably H_2CrO_4 and $H_2Cr_2O_7$, and that these compounds are dissociated to a large extent in the solution.

XXXV.—*The Specific Rotatory and Cupric Reducing Power of Invert Sugar and of Dextrose obtained from Cane Sugar by means of Invertase.*

By JAMES O'SULLIVAN.

HITHERTO the numbers published for the specific rotatory and cupric reducing power of invert sugar and of the dextrose prepared from invert sugar have been determined from the products obtained from a solution of cane sugar by heating it with an acid.

Herzfeld, Bornstein, and Winter (*Ber.*, **18** and **19**) have thrown considerable doubt on Dubrunfaut's number $[\alpha]_j = -106°$ for levulose by the isolation of crystalline levulose prepared from inulin and cane sugar, which they say has only an $[\alpha]_j$ C 20 per cent. at $20° = -83$.

Dubrunfaut's well known numbers (*Compt. rend.*, **42**, 901) are—

$$[\alpha]_j \text{ T } 14° = -106°;\ \text{T } 52° = -79·5°;\ \text{T } 90° = -53°.$$

If we take the first number $-106^{14°}$, and apply Montgolfier's ratio $[\alpha]_j : [\alpha]_D = 1·129 : 1$, we get $[\alpha]_D = -93°$.

The following numbers are also given for levulose:—Neubauer (*Ber.*, 1877, 829), $[\alpha]_D^{14°} = -100°$; Jodin (*Compt. rend.*, **58**, 613), $C = 5$ per cent., $[\alpha]_D = -93°$; Kiliani (*Ber.*, **14**, 2530), $C = 1$ to 4 per cent., $[\alpha]_D = -92—93°$; Rotondi and Zecchini (*Deutsche Zucker-indust.*, 1887, 1091), $[\alpha]_D = -100°$; and, finally, M. Honig and J. Jesser (*Monatsh. Chem.*, **9**, 562—578) give for levulose, which they prepared by the same method as Herzfeld and Winter, $[\alpha]_D^{15\cdot4°} = -93\cdot526°$.

Tuchmid (*J. pr. Chem.*, **2**, 235) gives for a solution of invert sugar with $C = 17\cdot21$ per cent. at 0° $[\alpha]_D = -27\cdot9°$, and that this value decreases with increase of temperature according to the formula $[\alpha]_D^t = (-27\cdot9° - 0\cdot32°t)$.

Dubrunfaut found for invert sugar—strength not stated (*Compt. rend.*, **42**, 901), T 14° $[\alpha]_D = -23\cdot6°$, which, by allowing for 14° of temperature, we obtain at 0° $(-23\cdot6° - 0\cdot32° \times 14) = -28°$, a number which agrees with Tuchmid's.

Maumené (*Compt. rend.*, **80**, 1139) says that invert sugar possesses similar properties only when the proportions of water and acid, the temperature and duration of the action, and the mode of neutralisation employed have been strictly identical.

It is evident that if Herzfeld's number for levulose be correct, invert sugar cannot be composed of equal parts of levulose and dextrose possessing the rotatory powers usually ascribed to them.

I intend to record in this paper that invert sugar, obtained from cane sugar by means of invertase, has a specific rotatory power T 15·5° $[\alpha]_j = 24\cdot5°$, and that it yields a dextrose with an $[\alpha]_j = 57—58°$, and that both have the same cupric reducing power.

As far back as 1878, it was found necessary, in quantitative analytical work, to discard the use of acid for the inversion of small quantities of cane sugar in mixtures containing substances which were acted on by acids, and to employ a method of inversion which would have no influence on these bodies. Invertase prepared from yeast presented itself as an inverting agent which was free from this disadvantage. Before invertase could be used it was necessary, first, to prove that cane sugar could be completely inverted by it, and also to determine what were the properties of the inverted product. As the numbers obtained have a bearing upon the rotatory power of levulose and upon the optical and cupric reducing methods of estimating cane sugar, I shall now give the method by which they were obtained.

The faces of a number of large and clear crystals of white sugar candy were carefully cleaned with a dry towel, and the crystals were then finely pulverised in an agate mortar. The pulverised sugar was kept in a stoppered bottle. At the same time some of the same sugar, which had been dissolved in water and crystallised from ethyl alcohol (0·80), was similarly treated. 3·292 grams of the first-mentioned sugar were taken, and it was found to lose nothing by drying, first, over sulphuric acid in a vacuum, and then in a current of dry air at 100°. It was dissolved in about 25 c.c. of cold water, which had been previously boiled. This solution weighed 30·463 grams, and its sp. gr., as determined in a Sprengel's tube, was found to be 1043·35 at 15·5°/15·5°. In the weighed solution there were 3·292 grams of sugar; therefore, in 100 c.c. of the solution there were 11·261 grams $\left[\frac{104{\cdot}335 \times 3{\cdot}292}{30{\cdot}463} = 11{\cdot}261\right]$. This gives a divisor of 3·85 for the 11·261 per cent. solution $\left[\frac{43{\cdot}35}{11{\cdot}261} = 3{\cdot}85\right]$.

The opticity of this solution in a 200 mm. tube of a Soleil-Ventzke-Scheibler polariscope, was found to be 43·3 divisions. As 0·384° of angular rotation is equal to 1 division of rotation on this instrument, and the 200 mm. tube was used, the specific rotatory power will be $[\alpha]_j = +73{\cdot}8^\circ$ $\left[\frac{10 \times (43{\cdot}3 \times 0{\cdot}384)5}{11{\cdot}261} = 73{\cdot}8\right]$.

The divisor then for the cane sugar employed and its specific rotatory power were

$$C = 11{\cdot}261. \quad D = 3{\cdot}85. \quad [\alpha]_j = 73{\cdot}8^\circ.$$

To 25·839 grams of this solution 0·03 gram of invertase (water deducted) was added, and the solution was digested for 17 hours at a temperature of 14—16°. The small thermometer used was washed with water, and the solution was again weighed. It weighed 29·261 grams, and its sp. gr., taken as before, was found to be 1040·71, and its opticity 200 mm. = −13, T 15·5°, which did not diminish after standing for 48 hours. In the 29·261 grams of solution there was 0·03 gram of invertase, therefore, in the 104·071 grams (100 c.c.) there was 0·106 gram.

The total rotation observed for the solution is −24·96°, $(-13 \times 0{\cdot}384)5$, and the total sp. gr. 1040·71.

The sp. gr. due to the invertase in the 100 c.c. of solution is 0·424 (1 gram of invertase in 100 c.c. = 1004); therefore, 1040·286 is the gravity due to invert sugar in the 100 c.c.

The specific rotatory power of the invertase was $[\alpha]_j = 31{\cdot}2^\circ$; then the rotation due to 0·106 gram is 0·33°.

The gravity due to the invert sugar, 1040·286 ÷ 3·85 = 10·463 grams in 100 c.c., and the total rotation −24·96° + 0·33°, due to invertase, gives −25·29° for the 10·463 grams of invert sugar, or an $[\alpha]_j = -24{\cdot}1^\circ$, $\left[\frac{25{\cdot}29}{10{\cdot}463}\right]$.

The cupric reducing power of the invert sugar was determined by O'Sullivan's modified gravimetric method (Trans., 1876, ii, 130), a weighed quantity of the solution being used, and it was found to be $K = 101$.

There are, in 100 c.c. of the solution of invert sugar, 10·463 grams, or in the 29·261 grams of the same solution there are 2·941 grams, which is the quantity of invert sugar produced by 2·788 grams of cane sugar employed $\left[\frac{25{\cdot}839 \times 11{\cdot}261}{104{\cdot}335} = 2{\cdot}788\right]$, or an increase of 0·153 gram.

10 grams of cane sugar on inversion, according to the equation

$$C_{12}H_{22}O_{11} + OH_2 = C_6H_{12}O_6 + C_6H_{12}O_6,$$

requires 5·26 per cent. of an increase, due to hydration, and the above increase amounts to 5·5 per cent.

In another experiment in which I employed the cane sugar crystallised from alcohol, and operated in a similar manner in every way to that I have just described, I obtained the following numbers:—

Specific rotatory power of the cane sugar, $C = 11$ per cent.; $[\alpha]_j = 73{\cdot}7°$.
Divisor for solution of gravity, $1043{\cdot}35 = D\ 3{\cdot}85$.
Specific rotatory power of the invert sugar, $C = 11{\cdot}4$ per cent.; $[\alpha]_j = -24{\cdot}8°$.
Cupric reducing power of the invert sugar, $K = 99{\cdot}0$.
Hydration in per cent. on cane sugar, 5·5.

It will be observed that in order to obtain the amount of invert sugar present in the solution after inversion, that the total gravity, less the gravity due to the invertase present, is divided by 3·85. That this number, although slightly high, is practically correct, I have just recently proved.

An experiment was made, as before, with large crystals of cane sugar, and gave the following numbers:—

Specific rotatory power of the cane sugar, $C = 15{\cdot}481$; $[\alpha]_j = 73{\cdot}2°$.
Divisor for solution of cane sugar of gravity $1059{\cdot}5 = 3{\cdot}84$.
Specific rotatory power of the invert sugar, $C = 14{\cdot}07$; $[\alpha]_j = -24{\cdot}5$.
Cupric reducing power of the invert sugar, K, $I = 99{\cdot}2$; $II = 99{\cdot}4$.
Hydration in per cent. on cane sugar, 5·4.

A weighed quantity of the inverted solution of this experiment was evaporated in a strong glass test-tube provided with a rubber plug, through which passed two glass tubes, one of which connected the tube with a suction pump and the other with an air-drying apparatus. The tube was immersed in a salt-water bath kept boiling at 104° whilst the pump was working. In this manner the water was removed at a diminished pressure (100 to 120 mm.). When the syrup ceased to bubble in the tube an extremely gentle current of dry air was allowed to enter through the second tube, which was kept closed till then. This current of air was so slight that it did not materially influence the pressure. The tube and its contents were weighed from time to time until three consecutive weighings, made four hours apart, were found to be the same. The weight of the glass tube, after the experiment, was found to have diminished 0·004 gram.

4·62 grams of the inverted solution, which had a total gravity of 1054·26, were found to leave, when dried in this manner, 0·622 gram of dry substance, or 100 c.c. contains 14·193 grams, $\left[\frac{105\cdot426 \times 0\cdot622}{4\cdot62}\right]$. In the 100 c.c. of solution there was 0·117 gram of dry invertase; therefore 14·193 − 0·117 = 14·076 grams of invert sugar. The total gravity 1054·26 − 0·462, due to invertase, is 1053·798 due to invert sugar. Now, 53·798 ÷ 14·076 = 3·82, the divisor for the invert sugar solution mentioned in the last experiment. The numbers given for the invert sugar in that experiment are worked out from this divisor, and it will be seen that they do not practically differ from the numbers given for the other experiments in which the divisor 3·85 was used.

Three inversions of cane sugar were made with very small quantities of invertase, in order to see if, by employing the number $[\alpha]_j = -24\cdot5°$ for the cupric-reducing power of the inverted solution and $[\alpha]_j = 73\cdot8°$ for the non-reducing substance, the observed $[\alpha]_j$ for the inverted product would agree with the calculated number. The following are the results:—

		Observed $[\alpha]_j$.	Calculated $[\alpha]_j$.
Exp. I.	K = 95·73 per cent.	−21·1°	−20·3°
,, II.	,, = 95·00 ,,	−21·6	−19·7
,, III.	,, = 97·53 ,,	−21·6	−22·0

The experiments mentioned, together with these results, prove pretty conclusively that in the optical and cupric reducing method of estimating cane sugar, the numbers $[\alpha]_j = -24\cdot5°$ and K 100 per cent. for the invert sugar are correct.

In a 200 mm. tube of a Soleil-Ventske-Scheibler polariscope, 1 gram of cane sugar in 100 c.c. of solution gives a rotation of 3·84 divisions, and 1 gram of invert sugar gives −1·27 divisions. Theoretically, 1 gram of cane sugar yields 1·0526 grams of invert sugar; therefore, if the volume of the solution is kept constant, the true optical loss in a 200 mm. tube, which 1 gram of cane sugar, after inversion, will show, is 3·84 − (−1·27 × 1·0526) = 5·18 divisions. From this it will be seen that the loss in opticity per 100 c.c. of a cane sugar solution inverted either partially or completely by invertase, divided by 5·18—the 200 mm. tube being used—will give, in grams, the amount of cane sugar and which has been inverted.

To prepare dextrose from cane sugar by means of invertase, 100 grams of pure white sugar-candy were dissolved in about 300 c.c. of boiling water; when cold, 0·3 gram of invertase was added to it, and after well agitating the solution it was laid aside for four days. On the fourth day, a portion of the solution was diluted, and, on analysis, the sugar in solution was found to have $[\alpha]_j = -23·6$. On the sixth day the whole of the remaining portion of the solution was evaporated under a diminished pressure to about 80 c.c. This syrup was laid aside, and in about a week a large crystallisation had taken place. This crystalline mass was washed with alcohol of 0·82, and then dried upon filter paper. The crystals thus obtained appeared to have no syrupy matter mixed up with them, and, in fact, from their appearance, I fancied that I had a fairly pure dextrose. This, however, was not so, for on dissolving some in water and boiling off the alcohol I found, in a 5 per cent. solution, the $[\alpha]_j = 12°$. By repeated washing by decantation with alcohol, crystals were left which were much whiter than the original, and which, on analysis of a portion, gave C 3 per cent., $[\alpha]_j = 54°$. The whole of the remaining crystals was dissolved in about 20 c.c. of water and to this solution 20 c.c. of dry methyl alcohol was added. In 17 days, the crystals that had formed were removed from the mother liquor and were washed on a filter with methyl alcohol. Only 7 grams of crystals were obtained, as I aimed at the first crystallising portion. These crystals were white, clear, large, and well defined. After drying over sulphuric acid in a vacuum for 48 hours, the portion taken was weighed, and it amounted to 4·869 grams; on further drying in a current of dry air at 100° and finally in a vacuum, the weight was found to remain constant. It was dissolved in about 20 c.c. of water, and its opticity and divisor determined in the same manner as that employed in the case of cane sugar. The numbers yielded were :—

T 15·5°. C = 19·628. D = 3·8. $[\alpha]_j = 57·1°$.
,, C = 10·095. D = 3·84. $[\alpha]_j = 57·2°$.
K, I = 99·5°; II = 100·5°.

I might mention here that I prepared dextrose from honey in a similar manner and obtained for two preparations, one crystallised from water, the other crystallised from alcohol, the following numbers :—

I. Crystallised from Water.

T 15·5°. C = 17·061. D = 3·8. $[\alpha]_j = 59·0°$.
„ „ = 10·844. „ = 3·79. „ = 58·5.
„ „ = 6·969. „ = 3·83. „ = 58·4.
„ „ = 3·521. „ = 3·85. „ = 56·0.

II. Crystallised from Methyl Alcohol.

T 15·5°. C = 14·000. D = 3·8. $[\alpha]_j = 58·5°$.
„ „ = 7·300. „ = 3·83. „ = 57·6.
„ „ = 3·890. „ = 3·85. „ = 56·0.

As the specific rotatory power of invert sugar, obtained by means of invertase where levulose is not acted on, is $[\alpha]_j = -24·5°$, and that of the dextrose prepared from it is $[\alpha]_j = 57°$, the apparent specific rotatory power of levulose calculated from these numbers must be $-24·5° \times 2 + 57° = [\alpha]_j = -106°$, $[\alpha]_D = -93·8°$; invert sugar being composed of equal portions of levulose and dextrose.

XXXVI.—*A Lecture Experiment to Illustrate the Phenomena of Coal Dust Explosions.*

By T. E. THORPE, F.R.S.

THAT the dust which is incidentally formed in the operations of coal getting, and which, therefore, is to be found in greater or less quantity in all collieries, can, under certain conditions, create or augment a colliery explosion, is now very generally admitted. But all mining men are not agreed as to the particular part which the dust plays in the explosion. Some mining engineers and colliery managers are disposed to regard its action as wholly secondary: they believe that it is only in the presence of fire-damp that the coal dust can be ignited by any of the agencies which may initiate an explosion, and that even when ignited its explosive combustion is quickly arrested if the supply of fire-damp ceases. Whilst it is now allowed on all hands that air containing so small a proportion of fire-damp as to be non-explosive may, when mixed with coal dust sufficiently finely divided and containing a sufficiently large amount of combustible matter, become explosive, many engineers and coal mine inspectors of great skill and experience are of opinion that coal dust alone, that is, in the complete absence of fire-damp, may give rise to violent explosions. Indeed, it is very difficult to resist the evidence which has been accumulated by Mr. William Galloway, the Messrs. Atkinson, and others, in support of this view, which derives a *primâ facie* support from the explosions which have been known to occur in flour mills, where, as in the well-known cases of the Annapolis Mills, in America, and the Tradeston Mills, at Glasgow, sparks from the stones have ignited the fine flour or stive dust, and the buildings have, in consequence, been blown down.

Of late years a number of colliery explosions have been investigated with very special care, with the result that, when the conditions under which the catastrophes occurred are considered, it seems impossible to resist the conviction that in some, at least, of these cases, the explosion originated in air absolutely free from fire-damp, and that it was propagated by dust thrown by concussion or vibration into the air of the ways and working places of the mine. So long as dust was present, or could be thrown into the air, so long would the explosive wave continue and gather force. Indeed, there is a gradually growing belief in the mining world that the violent explosions, such as those of Abercarn, Risca, Seaham, and Penygraig, which are found to ramify throughout the pits, and to penetrate into almost every part of them, are to be attributed to coal dust rather than to fire-damp, which latter cause necessitates either the assumption of sudden and simultaneous outbursts of gas over a large area of the mine, and often, too, when there is no other ground for assuming such outbursts; or a state of ventilation such as is never possible in a well regulated pit. It is significant, too, that violent explosions of this class seldom occur in very wet pits, although such pits may, and very frequently do, contain considerable amounts of fire-damp.

It has long been recognised that a large proportion of these accidents are connected with the use of explosives, and more particularly gunpowder, employed in making roadways or in driving headings, or in getting down the coal. In the course of a year a great number of "shots" are fired in a mine, and, for the most part, of course, with impunity. But it occasionally happens, either because the shot is overcharged, or because the tamping or stemming is badly or carelessly done, that the "shot" is blown out, and the explosive spends its energy in driving out the tamping, when there is a violent concussion in the air and a loud report—a mass of flame shoots from the hole—particularly when gunpowder is employed, and the suspended dust ignites, and is consumed with great suddenness. The violent movement of the air dislodges fresh dust from the floor, the roof, and the timbers, and through this the flame is propagated, and continues so long as it is fed with the finely-divided combustible matter.

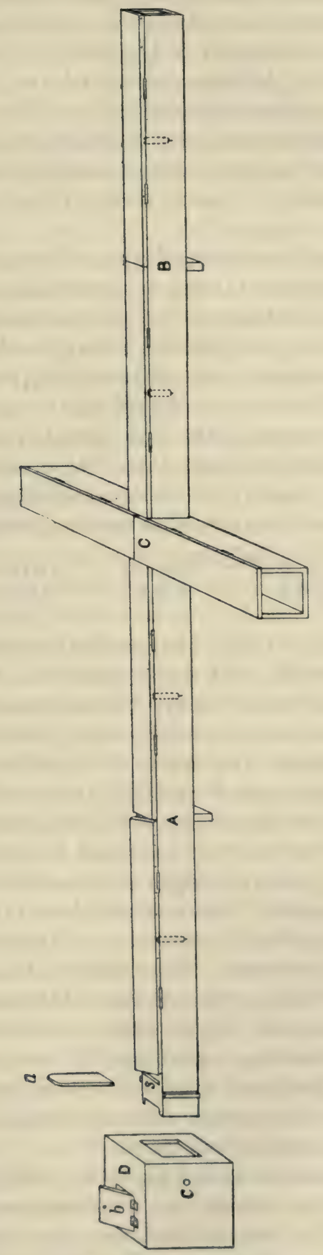
A blown out or overcharged "shot" may then produce an explosion, either by igniting an explosive mixture of gas and air, which, by the concussion, raises a cloud of dust, which, in its turn, burns with explosive violence; or the flame of the shot may directly ignite the dust without the intervention of fire-damp.

For some years I have been in the habit of illustrating the general phenomena of a dust explosion to my class by means of an apparatus devised on the principle of that adopted by Mr. Galloway in his experiments at Llwynpia.

It consists of a long, narrow box, A and B, made in two pieces, which together are 12 feet in length and 5 inches deep and 5 inches wide externally. Each length of the longer box fits into the sides of a similar box C, 6 feet long, which serves as a cross gallery, and illustrates how the explosion may travel through all parts of the pit so long as it is fed with dust. The boxes are open at both ends, and fitted at the top with lids attached by strong hinges and hasps. They are strengthened across the top by cross-pieces, and should be strongly made, best of 1-inch oak, and should be put together with screws. At one end of the longer box is a well-fitting shutter or slide *a*, working through a slot *s*, and in grooves at the sides. This end of the long box is inserted into one side of the quadrangular box D, 9 inches square, which is also fitted with a lid *b* at the top. At *c* is a small hole, through which can be inserted a caoutchouc tube from a gasometer filled with marsh gas or coal gas. A graduated bell-jar, furnished with a stopcock and suspended in a wider jar containing water, is, on the whole, the most convenient arrangement for delivering such an amount of the gas into the box as will form an explosive mixture with the air contained in it.

A small quantity of coal dust is then strewed on the bottom of the boxes, along their entire length, and the lids are fastened down by means of the hasps. To illustrate the direct action of the blown out shot, the barrel of a small pistol, charged with a blank cartridge, is inserted through the lid *b*. On firing the cartridge the dust cloud, consequent on the explosion, is ignited, and a flame, often several feet in length, is projected from the further end of the box.

To imitate the effect of a local explosion of fire-damp, the wooden shutter *a* is dropped down through the slot *s*. The quantity of gas, either marsh gas or coal gas, required to make an explosive mixture (determined by previous trial) is then delivered through the hole *c*, the lid *b* being of course closed. On drawing out the shutter *a*, and thrusting a lighted taper either through the slot *s* or through the hole *c*, the explosion instantly creates a cloud of coal dust, which, by its violent ignition, raises a continuous cloud along the whole length of the box through which the flame is propagated,


B
C
A
a
S
D
b
C°

and is driven out at the further end, often to a distance of 4 or 5 feet. The success of the experiment seems to depend upon the nature of the coal dust and the character of the initial explosion. Some dusts do not readily rise by the concussion, and the flame travels only a comparatively short distance along the box. The hygrometric state of the air and of the dust also seems to affect the result. In order to obtain the dust in the proper state of subdivision, it must be sifted through very fine muslin or passed through a wire sieve made of the finest gauze.

For class demonstrations, lycopodium powder, or the spores of club moss (*Lycopodium clavatum*), used by pyrotechnists, and for the production of theatrical lightning, is a very good and cleanly substitute for coal dust, which, by its ignition, always makes a somewhat unpleasant smoke; moreover, it almost invariably happens that portions of caked or charred dust are projected on to the table or about the lecture room. The spores of the club moss have a composition more nearly approaching that of lignite than that of coal. From analyses made by Miss E. G. Hagerty in the laboratories of the Royal College of Science, 100 parts of the air-dried spores contain—

Carbon.	Hydrogen.	Nitrogen.	Oxygen.	Ash.
68·09	9·79	1·22	18·90	2·00

With this substance, all the characteristic phenomena of a dust explosion may be readily and easily observed. Indeed, the use of lycopodium powder allows of many of these phenomena to be investigated with more ease and certainty than when coal dust itself is employed. For example, the track of a colliery explosion is now traced by the peculiar manner in which the caked or charred dust is lodged or thrown on to the pit props, timbers, or other objects in the path of the explosive wave or air rush, and it is by following up these indications that the point of origin and cause of the explosion can frequently be ascertained. The charred dust is found to be lodged in greatest proportion *behind* the obstacle, and not on the face presented to the advancing air current. The cause of this is easily explained by the formation of eddies, which drive in the dust to the rear of the object. This phenomenon may be readily illustrated in the arrangement described, by inserting small pegs of wood along the bottom of the box, when it will be found, after the explosion, that the lycopodium has been swept away in a regular and symmetrical manner before the face of the peg, and heaped up at its rear.

It is well known that a colliery explosion, and, particularly, a dust explosion, increases in violence as it progresses. At its point of origin the evidences of disturbance are often comparatively few; lamps, tools, clothes, &c., are frequently found in the position in which they have been left by their owners, whereas, hundreds of yards away, the signs of havoc and destruction are on every hand; stoppings, screens, and brattices are blown down, wagons are hurled together, and, in some cases, every shred of clothing, even to the clogs or shoes, has been stripped from the bodies of the men. The gradually increasing violence of the explosion is well illustrated by the increasing areas of clear space before the pegs, as the flame travels to the end.

It has been frequently noticed that inflammable or readily ignitable substances are left untouched or unconsumed by the flame which traverses the ways of the mine: *e.g.*, the powder in the bottles or canisters used by the men, although freely exposed, and in the neighbourhood of the shot holes, is often unburnt. If little heaps of fine powder are placed at intervals along the box in the track of a dust explosion, it will be found that they are rarely fired. Small pieces of touch-paper are seldom ignited, and then only near the open end of the box where the flame is strongest. Gun-cotton, however, is ignited in all parts of the track.

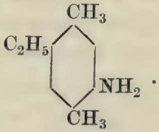
It has been asserted that in a colliery explosion the rush of air is frequently so violent, and the consequent diminution of pressure in parts so great, that the occluded fire-damp may actually be drawn from the face of the coal, and thereby feed, so to say, the explosion. It would appear from the evidence published in the First Report of the Royal Commission on Explosions from Coal Dust in Mines that this so-called "Suction Theory" is held by many colliery managers. So far as I know, the only experimental proof of it hitherto advanced is cited in a paper by Mr. G. C. Greenwell, F.G.S., published in the *Transactions of the Manchester Geological Society.* I am indebted to Mr. Greenwell for a sketch of the apparatus he employed. It consisted of a box, closed at one end and open at the other, about 3 feet long. At right angles to this box, and opening into it, was a second and smaller box, fitted with a valve, on which the pressure of the outer air could act. On firing a shot at the closed end of the longer box, the violent rush of air towards the open end dragged out more or less of the air from the box placed at right angles, and the valve was driven inwards. This, of course, is what might have been expected. The lateral current acts as in the injector or in the "spray producer," or as in the case of the current of coal gas emerging from the jet of the Bunsen lamp. By means of a manometer constructed on the same principle as that by which I demonstrated some years ago (Trans., 1877, i, 627) the area of low pressure, near the jet of a Bunsen lamp, when the gas is turned on, and, in consequence of which air is driven in through the holes at the base, I have sought to gain evidence of the existence of a diminution of pressure along the sides of the gallery during the course of a dust explosion. The manometer was placed at different parts of the apparatus during successive explosions, but there was not the slightest indication of such a diminution; on the contrary, there was always a strong pressure against the sides and top of the box, exactly opposite to that which the suction theory requires.

XXXVII.—*On Some New Bases.* Part I. *Ethyldimethylamidobenzene*, $C_{10}H_{15}N$ [$C_2H_5 : CH_3 : CH_3 : NH_2 = 6 : 1 : 4 : 3$].

By W. R. Hodgkinson and Leonhard Limpach.

Numerous bases having a composition expressed by the formula $C_{10}H_{15}N$ are already known; they are included under (1) amidoisobutylbenzenes; (2) several isomeric amidomethylpropylbenzenes or cymidines; (3) several isomeric tetramethylbenzenes; and (4) the one we now describe, ethyldimethylamidobenzene or ethylxylidine.

The new base has been obtained by heating pure paraxylidine hydrochloride, $C_8H_{11}N,HCl$, with ethyl alcohol at a high temperature, 250—300°, in an autoclave. It has been already shown by one of us (L. Limpach, *Ber.*, **21**, 640) that under this treatment the alkyl molecule joins on to the benzene molecule, in the first instance entirely in the para-position relatively to the amido-group; consequently the new base will have the constitution



As, however, after the substitution of ethyl for the hydrogen in the para-position relatively to the NH_2 group in the original xylidine, ethyl can then be substituted for the ortho-hydrogen atom next to the NH_2 group, the formation of a certain amount of diethyldimethylamidobenzene cannot be avoided when this method is employed. The presence of this second base adds, consequently, to the difficulty in purifying the first.

Preparation.

The method of preparation finally adopted was to heat 1 gram-molecule of dried paraxylidine hydrochloride with 1 gram-molecule of ethyl alcohol in an autoclave at 250—300° for five or six hours, the pressure rising rapidly after the commencement of heating to between 30 and 35 atmospheres, this pressure being maintained during the whole time of heating. On cooling, a small quantity was taken out, dissolved in very dilute hydrochloric acid, and the solution treated with sodium nitrite to test for secondary bases. In cases where a strong milkiness was produced (nitrosamines), the content of the autoclave was further heated for several hours, a little higher than before, nearly to 300°, in order to convert as much as possible of the secondary base into primary. The product was then dissolved in hot water with a very little hydrochloric acid, filtered from a small quantity of tarry matter, made slightly alkaline, and the bases distilled off with steam. The oil thus obtained consists of primary, secondary, and tertiary bases. It was fractionally distilled, the main product passing over between 235° and 260°. This fraction was employed for the preparation of the pure base.

After a few experiments, it was found that the best method of separating the secondary and tertiary bases and the diethyldimethylamidobenzene from the base sought was to convert the whole of them into sulphates. The sulphate of the new base is exceedingly insoluble in water, and therefore admits of being very easily separated from the accompanying bases. Instead of further fractionating, 150 grams of the fraction boiling between 235° and 260° were dissolved in a mixture of 50 grams of sulphuric acid and 100 c.c. of water, the bases being slowly added to the acid mixture. The sulphate of the new base separated out almost at once in leafy crystals, which were easily separated from the soluble sulphates by draining and pressing. The crystals were redissolved in a very large quantity of boiling water, again allowed to crystallise, and then treated with sodium hydrate, and the base distilled over with steam. At this stage of purification, the base itself distilled between 245° and 248°. Traces of paraxylidine were, however, still present, lowering the boiling point. For final purification, it was converted into the formyl compound, which was repeatedly crystallised from weak alcohol.

The formyl compound crystallises in long, silky prisms, and melts at 104—105°.

Analysis :—

0·2450 gram of substance gave 0·1890 gram H_2O and 0·6680 gram CO_2.

	$C_{11}H_{15}NO$.	Found.
H..........	8·47 per cent.	8·57 per cent.
C..........	74·57 ,,	74·4 ,,

From this formyl compound the pure base was obtained by hydrolysing it with dilute sulphuric acid, rendering alkaline with sodium hydrate, and steam distilling. As thus obtained, the pure base boils at 247° (thermometer in vapour); relative weight, 0·9635 at 15°; and remains liquid when cooled to $-10°$.

Analysis :—

0·2185 gram of substance gave 0·1980 gram H_2O and 0·6455 gram CO_2.

	$C_{10}H_{15}N$.	Found.
H..........	10·06 per cent.	10·07 per cent.
C..........	80·53 ,,	80·48 ,,

The acetyl derivative crystallises in brilliant prisms, and melts at 142—143°.

The sulphate, $C_{10}H_{15}N_2,H_2SO_4$, when pure, crystallises from boiling water in prisms. It is only very slightly soluble in water.

100 parts of a boiling saturated solution contain 1·14 parts of the sulphate; at 18°, 100 parts of water contain 0·55 part of the sulphate.

Analysis of the sulphate :—

0·5500 gram of substance gave 0·3262 gram $BaSO_4$ = 24·62 per cent. H_2SO_4. $C_{20}H_{30}N_2,H_2SO_4$ requires 24·74.

The hydrochloride, $C_{10}H_{15}N,HCl$, crystallises in prisms with 3 mols. H_2O. It is moderately soluble in water.

Analysis of the hydrochloride :—

0·2817 gram of substance lost, over sulphuric acid, 0·062 = 22·01 per cent. H_2O. $C_{10}H_{15}N,HCl,3H_2O$ requires 22·50 per cent.

0·2755 gram of the dried salt gave 0·2110 gram AgCl = 19·41 HCl per cent. Required 19·61.

The chloroplatinate forms long, fine needles which melt and decompose at 260°.

XXXVIII.—*Platinum Tetrachloride.*

By W. Pullinger, B.A., late Brackenbury Scholar of Balliol College.

This compound was first obtained by Norton (*J. pr. Chem.*, 1870, **2**, 469) in a hydrated form from the compound of silver chloride with platinum tetrachloride, discovered by Cammeille, and minutely studied by Jörgensen (*J. pr. Chem.*, 1877, **16**, 345). Norton tried to prepare the tetrachloride in an anhydrous state by heating the hydrated chloride in air. At 100°, he says, it loses 4 mols. H_2O, but the remaining molecule cannot be removed without decomposing the compound. He further attempted to obtain it by heating chloroplatinic acid, but without success. On this account he supposed that the elements of water were chemically combined with the platinum chloride, so as to form a compound $PtCl_2{<}\begin{smallmatrix}Cl_2H\\OH\end{smallmatrix}$, standing intermediate between chloroplatinic acid, $PtCl_2{<}\begin{smallmatrix}Cl_2H\\Cl_2H\end{smallmatrix}$, and platinum oxychloride, $PtCl_2{<}\begin{smallmatrix}OH\\OH\end{smallmatrix}$, a compound formed by the action of ammonia on the hydrated tetrachloride.

By adopting a new method, I have lately succeeded not only in obtaining the tetrachloride from chloroplatinic acid, but also in getting it anhydrous. The method is a simple one, suggested to me by Professor Lothar Meyer, of Tübingen. It consists in passing a stream of dry hydrogen chloride over heated, dry chloroplatinic acid. The latter was placed in a weighed porcelain boat, and this in a glass tube, which was heated in an air-bath. At the end of the experiment the boat was quickly transferred to a weighed tube, and was allowed to cool in a desiccator. The tube and its contents were then weighed. The platinum chloride was washed out of the boat and the solution evaporated to dryness in a platinum crucible. The platinum and chlorine were estimated in the residue by the usual methods.

In the first three experiments, the temperature ranged between 170° and 200°. In each case a small amount of dichloride was produced as shown by a slight darkening in colour of the chloride and by a small residue of dichloride remaining undissolved after the addition of water.

The analysis gave the following results:—

Expt.	1.	2.	3.	Mean.
Percentage of platinum ..	57·36	57·52	57·98	57·62
„ chlorine ..	41·32	41·24	40·65	41·07
				98·69

The percentages as calculated are:—

	$PtCl_4$.		$PtCl_4,H_2O$.
Platinum	57·86		(2) 54·92
Chlorine	42·14		39·99
		Water..	5·09
	100·00		100·00

A fourth experiment was made at 165°, the temperature of the bath being kept constant by a Harcourt's regulator. The heating was continued for 15 hours, as an appreciable amount of water was evolved after ten hours. The product obtained in this experiment was free from dichloride. The percentage of platinum found was 57·82, which agrees well with the theoretical value for $PtCl_4$.

As thus obtained, platinum tetrachloride is a very soluble, but not deliquescent substance. Its solution in water is strongly acid to litmus paper, and decomposes sodium carbonate rapidly with evolution of carbon dioxide.

These experiments show that platinum tetrachloride, $PtCl_4$, can be obtained by heating chloroplatinic acid at a temperature of 165° in a stream of dry hydrogen chloride.

Balliol College,
Oxford.

XXXIX.—*Separation of Arsenic, Antimony, and Tin.*

By John Clark, Ph.D.

About a year ago (*Journ. Soc. Chem. Indust.*, **10**, 444) I pointed out that arsenic could be estimated in alloys and minerals by means of ferric chloride; and I have now to lay before the Society the experiments which I have made to extend the use of ferric chloride to the separation of arsenic, antimony, and tin. With this object I prepared solutions of arsenious acid, antimony trichloride, and stannic chloride of known strength, and perhaps it is right that I should state that the strength of the antimony solution was determined by precipitating the metal as sulphide and drying the precipitate at 130°. For this investigation I have assumed that the trisulphide of antimony, dried at 130°, is pure Sb_2S_3. In my experiments, the above-mentioned solutions were mixed in various proportions, and, in order to imitate closely the conditions in which these metals are obtained in the ordinary course of a chemical analysis, the mixed solutions, in every case where the arsenic was estimated, were, in the first place, precipitated with sulphuretted hydrogen, and the precipitate washed with water. The mixed sulphides, while still moist, were then removed from the filter by piercing the bottom and washed into a distillation flask with 20 per cent. HCl (sp. gr. 1·10). Any traces still adhering to the filter were extracted by boiling with a little dilute caustic soda. When the filter is not separated from the precipitate, the paper is disintegrated and charred in the process of distillation, and some dark coloured organic compound is formed which interferes with the correct separation of the tin from the antimony.

Arsenic.—After the addition of the alkaline liquid with which the filter has been treated, an excess of ferric chloride, dissolved in strong hydrochloric acid, is added to the distillation flask. (The solution which I used for this purpose was made by dissolving 1 part of solid ferric chloride by weight in 5 parts of strong hydrochloric acid by volume, and the quantity employed contained about 3 parts of iron, in the form of ferric chloride, for each part of mixed sulphide.) The flask is then connected with a spiral glass condenser, to the end of which a straight chloride of calcium tube is attached, which dips into 3 or 4 ounces of pure water, and a funnel safety-tube is used to prevent the contents of the condenser passing back into the flask, and to enable fresh hydrochloric acid to be added without taking out the cork. The contents of the flask are then distilled to about one-fourth of their bulk, mixed with twice their volume of strong hydrochloric acid, and again distilled. To remove the last traces of arsenic, it is advisable to again add more strong hydrochloric acid, and distil as before. At the end of the third distillation, under these circumstances, the whole of the arsenic will have passed over into the condenser. The presence of arsenic is generally indicated during the distillation by the appearance of more or less of a yellow precipitate in the distillate and in the tube of the condenser. This precipitate consists of a mixture of sulphide of arsenic and sulphur, and is due to a little chloride of sulphur which distils off along with the chloride of arsenic, and, in contact with water, is decomposed into hydrogen chloride and thiosulphuric acid, which in its turn yields sulphur, sulphide of arsenic, and sulphurous acid. When the distillation is completed, the glass tube of the condenser is washed, first with water, and then with a little weak ammonia. The precipitate is separated from the condensed liquid by filtration, and the filter is washed with dilute ammonia, which dissolves the arsenic trisulphide, and leaves the bulk of the sulphur. The filtrate, which will contain some sulphide of arsenic, produced by the action of the hydrochloric acid on the ammoniacal solution of sulphide of arsenic, is then treated with excess of sulphuretted hydrogen, and the sulphide of arsenic is collected on a weighed filter, washed with water, then with methylated spirit, afterwards with bisulphide of carbon, and, finally, with methylated spirit. The filter and contents are then dried at 100°, and the arsenic weighed as arsenic trisulphide, As_2S_3.

Antimony.—The distillation flask, after the removal of the arsenic, contains the antimony as trichloride, and the tin as stannic chloride, mixed with ferrous and ferric chloride and separated sulphur. The contents are passed through a filter and washed with water.

Of the different methods which have been proposed for the separation of antimony and tin, Tookey's, which is based on the precipitation of the antimony by means of metallic iron, could very easily be applied; but, unfortunately, it has been found to be impossible to get correct results by this method on account of the readiness with which the precipitated antimony oxidises. Thiele (*Annalen*, **263**, 361) has shown also that when electrolytic iron is used, the whole of the tin is thrown down along with the antimony, even in the cold; and I have observed that thin sheet iron frequently precipitates more or less tin when the solution is concentrated. Loveton (*Jour. Pharm.*, **17**, 361) has pointed out that sulphide of antimony is less soluble in hydrochloric acid than sulphide of tin, and that, in solutions containing certain proportions of hydrochloric acid, the antimony and tin can be separated, quantitatively, by means of sulphuretted hydrogen. Loveton recommends the precipitation of the antimony in a solution containing half its volume of strong hydrochloric acid, and the collection of the precipitate on cotton wool to prevent the destruction of the filter by the hydrochloric acid, and he washes the sulphide of antimony precipitate with a mixture of 1 part of hydrochloric acid to 1½ parts of a saturated solution of sulphuretted hydrogen. Loveton operated only on alloys which he dissolved in hydrochloric acid with the assistance of nitric acid or potassium chlorate; and he states that the sulphides of antimony and tin are subsequently dissolved in sulphide of sodium, and electrolysed; but he does not give any results to show the accuracy of the process.

There can be no doubt, however, that in solutions containing certain proportions of hydrochloric acid, antimony can be completely separated from tin in this way; but when nitric acid or potassium chlorate is used to effect solution, it is not possible to know in what state of oxidation the antimony exists; so that it could not be weighed as trisulphide without further treatment.

When ferric chloride is used as the oxidising agent, the conditions are different, as in this case the antimony exists entirely in the form of trichloride, and the tin as stannous chloride. I have found, however, that in solutions containing half their volume of hydrochloric acid, it is difficult, in presence at any rate of ferric chloride, to precipitate the whole of the antimony; and when the solution is diluted so as to contain less than one-third of its volume of strong hydrochloric acid, the tin comes down if the current of sulphuretted hydrogen is continued in the cold after the whole of the antimony is precipitated. In solutions with about a third of their volume of hydrochloric acid, the process works fairly well in presence of ferric chloride, and the sulphide of antimony can be collected on an ordinary filter without danger.

Example.

	Taken.	Found.
Antimony	0·1310 gram.	0·1354 gram.
Tin	0·1169 ,,	0·1146 ,,
Total.......	0·2479 ,,	0·2500 ,,

The principal objection to Loveton's process, as carried out in this way, lies in the strict attention which must be paid to the proportion of acid and the necessity of washing with a mixture of hydrochloric acid and sulphuretted hydrogen water.

F. W. Clark (*Chem. News*, **21**, 124) has shown that stannic sulphide, SnS_2, is soluble in a strong solution of boiling oxalic acid, but according to Wittstein and A. B. Clark, jun. (*Zeit. anal. Chem.*, **9**, 490), the oxalic acid process does not give results of any value when applied to mixtures of arsenic, antimony, and tin. According to F. P. Dewey (*Zeit. anal. Chem.*, **21**, 14), the failure of the process in their hands is due to the presence of free mineral acid, and he recommends the neutralisation of the free acid, but finds it necessary to precipitate the antimony twice in a boiling oxalic acid solution to get it free from tin. From the results of my experiments, I am of opinion that Wittstein and Clark's failure could not be due to a moderate quantity of free hydrochloric acid, and I have come to the conclusion that when the antimony exists in the form of trichloride, and the tin in the stannic state, as in the present case, a combination of F. W. Clark's and Loveton's processes has advantages over either of them. The following are the details of this method :—The liquid from which the arsenic has been distilled is filtered to remove the sulphur, washed with water as far as necessary, then mixed with oxalic acid (about 20 parts of oxalic acid for 1 of mixed sulphides), dissolved in hot water, and sulphuretted hydrogen passed through the solution till it is cold. The solution should not be heated after the addition of the oxalic acid. Instead of passing the gas through the solution, excess of sulphuretted hydrogen water may be added; but in this case the antimony trisulphide precipitate should be filtered off shortly afterwards, as, on standing overnight, reduction takes place, and a little stannous sulphide is apt to be precipitated. In the presence of the oxalic acid and hydrochloric acid, only a portion of the ferric chloride is reduced, and the whole of the antimony is precipitated as antimony trisulphide, Sb_2S_3, absolutely free from tin, and mixed only with a little sulphur. The precipitate is collected on a weighed filter, and may be washed with any quantity of water without bringing down tin, and the filtrate gives no precipitate on the addition of a solution of sulphuretted hydrogen. After being washed with water, the precipitate is washed with alcohol, then with carbon bisulphide, and finally again with alcohol, the washings with alcohol and carbon bisulphide being kept separate. The filter and contents are dried, then digested in carbon bisulphide to ensure the complete removal of sulphur, and weighed as antimony trisulphide, Sb_2S_3; small precipitates do not require to be digested in carbon bisulphide.

In the experiments which I have made to test the accuracy of the process, the precipitates have in every case been dried, first at 100° and then at 130°, but I am of opinion that when the antimony sulphide is thoroughly dried at 100° the loss of weight at 130° is so minute that in the case of small precipitates at any rate it may be disregarded.

Example.

Sb_2S_3 dried at 100°.	Loss at 130°.	Loss per cent.
0·6648 gram.	0·0001	0·015
1·0020 ,,	0·0032	0·31
0·7348 ,,	—	—
0·7840 ,,	0·0026	0·33
	Average..........	0·14

In these experiments, the sulphide of antimony was in each case removed from the filter, and dried first at 100° before it was heated to 130°.

I am aware it is generally believed that antimony trisulphide retains a little water which is not given off till it is converted into the black sulphide, which takes place between 200° and 230°. Lesser even recommends that the sulphide of antimony should be heated to this temperature before it is weighed, but he found it took as much as nine hours to get a constant weight in a covered crucible. There can be no doubt that antimony trisulphide suffers a loss of weight between 200° and 230°, but I am of opinion that this is due not to water but to oxidation, for, although the loss is small when the sulphide is heated for a short time, it does not cease to lose weight when heated five or six hours daily for a week in an open vessel without the filter, and it gradually becomes brown in colour, and consists of a mixture of oxide and sulphide.

The following experiments show the extent to which oxidation takes place under these conditions:—

	Weight of Sb_2S_3 dried at 130° taken.	Loss in about 30 hours at 200°—230°.	Sulphur in residue.	Sb_2S_3 corresponding to the sulphur.
(*a.*)	0·7782 gram.	0·0657	0·0609	0·2157
(*b.*)	0·8187 „	0·0757	0·0525	0·1859

Sb_2S_3 per cent. in residue, (*a.*) 30·2 : (*b.*) 25·3.

These results indicate plainly that the antimony trisulphide is gradually converted into oxide when heated between 200° and 300°, and that it is of no use to heat the sulphide to this temperature. In my opinion, antimony trisulphide, dried at 130°, is anhydrous, and the most convenient form in which the metal can be weighed. I am also of opinion that it is less open to objection than any of the other forms in which antimony is frequently estimated. Bunsen (*Annalen*, **192**, 317) has pointed out that the temperature at which Sb_2O_5 is converted into Sb_2O_4 is so near the temperature at which the Sb_2O_4 is decomposed that he has given up this form as useless. It has also been recently shown by two independent observers, J. Thiele (*Annalen*, **263**, 361) and T. Wilm (*Zeit. anal. Chem.*, **30**, 428), that the pentsulphide of antimony obtained by Bunsen's process contains a considerable quantity of free sulphur, and I have referred to the objections to weighing antimony as metal.

Tin.—The filtrate from the antimony precipitate, from which the alcohol and carbon bisulphide washings are excluded, contains the whole of the tin mixed with salts of iron and oxalic acid. To destroy the latter, the solution is heated, and solid permanganate of potash is added in small quantities at a time, till a precipitate of oxide of manganese is obtained which does not redissolve on boiling. Some ferrous salt is added to dissolve the oxide of manganese, and a stream of sulphuretted hydrogen is passed through the hot solution till it is quite cold. Under these circumstances, the tin, mixed with sulphur, is precipitated in a condition sufficiently dense to enable the precipitate to be collected and washed with water without showing any tendency to pass through the filter. When thoroughly washed, the filter and contents are dried, and the tin converted by ignition into stannic oxide, SnO_2, in which form it is weighed.

The following are the results which I obtained by this method:—

No. I. Experiment with known quantities of antimony trichloride and stannic chloride in presence of oxalic acid and a considerable quantity of ferric chloride:—

	Taken.	Found.
Antimony	0·1310 gram.	0·1354 gram.
Tin	0·1170 „	0·1198 „
Total	0·2480 „	0·2552 „

No. II. Experiments on known quantities of arsenic, antimony, and tin, precipitated as sulphides, and afterwards treated with ferric chloride and oxalic acid as described:—

First. (With a small proportion of Arsenic.)

	Taken. Gram.	(A) found. Gram.	(B) found. Gram.	(C) found. Gram.
Arsenic.....	0·0157	0·0134	0·0174	0·0174
Antimony...	0·0655	0·0674	0·0646	0·0650
Tin.........	0·0568	0·0575	0·0560	0·0565
Total.....	0·1380	0·1383	0·1380	0·1389

Second. (With a small proportion of Antimony.)

	Taken. Gram.	Found. Gram.
Arsenic............	0·0628	0·0601
Antimony..........	0·0163	0·0158
Tin................	0·0585	0·0589
Total........	0·1376	0·1348

Third. (With a small proportion of Tin.)

	Taken. Gram.	Found. Gram.
Arsenic............	0·0628	0·0612
Antimony..........	0·0665	0·0646
Tin................	0·0146	0·0168
Total........	0·1439	0·1426

Fourth. (With larger quantities of the three Metals.)

	Taken. Gram.	Found. Gram.
Arsenic............	0·1310	0·1353
Antimony..........	0·1256	0·1253
Tin................	0·1169	0·1206
Total........	0·3735	0 3812

The only objection to the process which I have described is the necessity of digesting the sulphide of antimony with carbon bisulphide to remove the sulphur produced by the reduction of the ferric chloride. This difficulty can, however, be obviated by reducing the excess of ferric chloride before adding the oxalic acid. To effect this, I introduce a narrow strip of pure sheet iron into the solution after the removal of the sulphur and heat; reduction takes place in a few minutes. As soon as the yellow colour of the ferric chloride disappears, the undissolved iron is taken out; the antimony, which comes down to some extent before the ferric chloride is reduced, is removed by washing and rubbing, and to the solution containing the precipitate, the hydrochloric acid solution of ferric chloride is added drop by drop till the antimony dissolves, and the liquid acquires a permanent, yellowish tint indicating a slight excess of ferric chloride. The solution of oxalic acid (mixed in this case with about one-third of its bulk of hydrochloric acid) is then added, and the antimony precipitated with sulphuretted hydrogen, and washed with alcohol and carbon bisulphide, as already described.

Under these conditions, the quantity of free sulphur is so small that it is unnecessary to digest the precipitate with carbon bisulphide.

Example.

	Taken. Gram.	Found. Gram.
Antimony..........	0·1310	0·1302
Tin................	0·1170	0·1232
Total........	0·2480	0·2534

The hydrochloric acid is added to the oxalic acid solution to prevent the tin from being precipitated, as, in the absence of ferric chloride, tin is apt to come down along with the antimony sulphide when too little free acid is present.

These results indicate that the ferric chloride plays a very important part in the process; it is by its means that the antimony is always obtained in the form of trichloride. The ferric chloride also assists in preventing the precipitation of the tin, and renders it unnecessary to pay strict attention to the proportion of free acid.

For qualitative purposes, it is not necessary to employ a condenser in distilling off the arsenic; a bent tube dipping into water being sufficient, but it is advisable to use a safety-tube to prevent the distillate passing back.

In the case of alloys or antimony ore, the metal or mineral is dissolved in strong hydrochloric acid and ferric chloride, and the arsenic is distilled off at once. The sulphides of antimony and tin, after being separated from the other metals of the sulphuretted hydrogen group, are estimated as above.

XL.—*Decomposition of Mannitol and Dextrose by the* Bacillus ethaceticus.

By PERCY F. FRANKLAND, Ph.D., B.Sc. (Lond.), F.R.S., and
J. S. LUMSDEN, B.Sc. (St. Andrews).

IN previous communications, the fermentative changes brought about by this specific microbe, in suitable solutions of mannitol, glycerol, and calcium glycerate, have been described by one of us. It has been shown that in all these cases, almost the exclusive products, excepting the gaseous ones, are ethyl alcohol and acetic acid, together with varying proportions of formic acid and traces of succinic acid. The object of the present investigation was, firstly, to determine the nature of the gaseous products, and, secondly, to endeavour to ascertain the quantitative relationship existing between the various products of these fermentations, in the same manner as has been recently done by one of us for the fermentations induced by the *Pneumococcus* (Friedländer) in mannitol and dextrose.

The methods adopted were substantially the same as those described in the latter communication, a given quantity of the 3 per cent. solutions of mannitol and dextrose, respectively, being fermented in bottles provided with delivery-tubes, so as to admit of the collection of the evolved gases over mercury. The volume of gas evolved in each case was measured, and representative samples were submitted to analysis, whilst in the liquid left after fermentation was complete, the alcohol and volatile acids were determined, according to the methods already fully described.

Fermentation of Mannitol.

400 c.c. of a 3 per cent. solution of mannitol, to which the necessary nutritive materials had been added, were fermented with a pure culture of the *B. ethaceticus* at a temperature of 36°.

In the following table the volumes of gas collected during the course of the fermentation are recorded:—

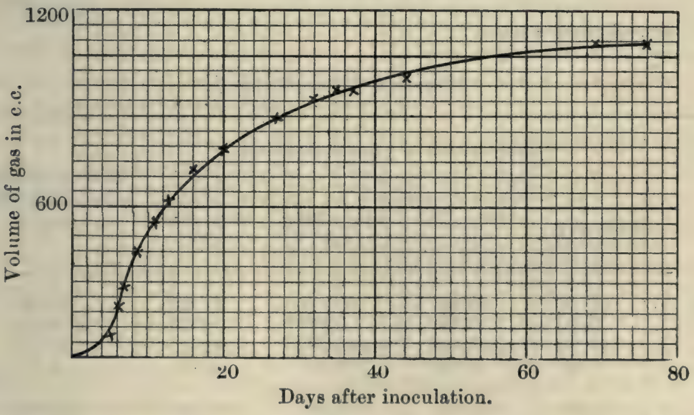
No. of days after inoculation.	Volume of gas.	Total volume of gas collected.
4	Tube (1) 28·4 c.c.	28·4 c.c.
4	,, (2) 37·0 ,,	65·4 ,,
4	*,, (3) 13·2 ,,	78·6 ,,
5	,, (4) 100·0 ,,	178·6 ,,
5	,, (5) 17·8 ,,	196·4 ,,
6	,, (6) 90·2 ,,	286·6 ,,

No. of days after inoculation.	Volume of gas.	Total volume of gas collected.
8	Tube (7) 131·2 c.c.	417·8 c.c.
10	„ (8) 116·0 „	533·8 „
12	„ (9) 89·0 „	622·8 „
15	*„ (10) 126·7 „	749·5 „
19	„ (11) 80·0 „	829·5 „
26	„ (12) 120·7 „	950·2 „
28	„ (13) 25·2 „	975·4 „
30	„ (14) 24·4 „	999·8 „
31	„ (14*a*) 21·4 „	1021·2 „
33	*„ (14*b*) 19·2 „	1040·4 „
36	„ (15) 29·8 „	1070·2 „
43	„ (16) 53·0 „	1123·2 „
68	*„ (17) 126·0 „	1249·2 „
75	„ (18) 7·8 „	1257·0 „

Thus, the total volume of gas collected amounted to 1257 c.c.

The progress of the fermentation is most clearly indicated by means of the following graphic representation, in which the abscissæ denote lapse of time in days since inoculation, and the ordinates, the volume of gas measured in cubic centimetres:—

Fermentation of Mannitol.



Mr. McCowan, B.Sc., Lecturer on Mathematics and Physics in University College, Dundee, has again most kindly come to our assistance in the investigation of the mathematical properties of this curve, of which he finds the equation to be

$$v = \frac{11{\cdot}1t^2}{1 + 0{\cdot}049t + 0{\cdot}00843t^2},$$

in which $v =$ volume of gas in cubic centimetres, and $t =$ time in days from the date of inoculation.

The manner in which the curve fulfils the conditions of this equation may be gathered from the following comparisons of the results of calculation and observation:—

Day.	Volume of gas (calculated from equation).	Volume of gas (observed).
5	190 c.c.	78·6 c.c.
10	475 ,,	480·0 ,,
20	829 ,,	829·5 ,,
30	994 ,,	990·0 ,,
40	1080 ,,	1090·0 ,,
50	1131 ,,	1170·0 ,,
60	1162 ,,	1210·0 ,,

Thus, just as in the case of the curve representing the evolution of gas in the fermentation of mannitol by the *Pneumococcus*, the results of observations are below those of calculation at the beginning, and above them at the close, of the fermentation, which is doubtless, to a great extent, due to the absorption of carbonic anhydride by the liquid at the commencement, and by the continued decomposition of bicarbonate of lime at the termination of the process.

Samples of the gas thus given off were submitted to analysis, and in the preceding table (pp. 432—433) the tubes selected for examination are marked with a *.

Mannitol Fermentation.

	Composition of gases evolved on				Mean (excluding that of the 4th day).
	4th day.	12th—15th day.	31st—33rd day.	43rd—68th day.	
CO_2	47·36	58·03	60·50	57·26	58·59
O	0·30	0·06	0·06	0·32	0·15
H......	48·76	41·89	39·36	42·20	41·15
N......	3·58	0·02	0·08	0·22	0·11
	100·00	100·00	100·00	100·00	100·00

The gaseous products are thus exclusively carbonic anhydride and hydrogen, just as has already been shown to be the case in the fermentation of mannitol with the *Pneumococcus* (Friedländer); moreover, as in that case also, the gases are given off in about the proportion of 6 volumes or molecules of carbonic anhydride to 4 volumes or molecules of hydrogen. In taking the average above we have, of course, excluded the gas collected on the fourth day, when air was still present, and when absorption of carbonic anhydride by the liquid was obviously still going on.

In the liquid, after the fermentation was completed, the alcohol and volatile acids were determined as previously described; the alcohol being first oxidised with potassium dichromate and sulphuric acid, and the acetic acid so formed being then converted into barium salt, whilst the volatile acids were also converted into barium salts, weighed, and analysed.

Thus the acid obtained by oxidation of the alcohol yielded 3·3835 grams of barium salt, yielding 90·92 per cent. $BaSO_4$.

This corresponds to 1·221 *gram of ethyl alcohol.*

The volatile acids gave 1·601 gram of barium salt, yielding 97·46 per cent. $BaSO_4$, corresponding to

0·8652	gram of barium	formate	= 0·3505	gram of	formic acid.
0·7358	,, ,,	acetate	= 0·3463	,,	acetic ,,
1·6010					

As regards the gaseous products, assuming the whole of the 1257 c.c. of gas collected to have the composition indicated by the average figures given above (58·59 per cent. CO_2, 41·15 per cent. H), there would be 736·6 c.c. of carbonic anhydride or 1·452 gram, and 517·9 c.c. of hydrogen or 0·046 gram. Of the above carbonic anhydride, it can be calculated that 0·2946 gram is due to the decomposition of calcium carbonate by the acetic and formic acids liberated, whilst the remaining 1·1574 gram is due to the actual fermentation of the mannitol. As recently pointed out by one of us (this vol., p. 270), the whole of the hydrogen with its molecular equivalent of carbonic anhydride may in these fermentations be referred to a preliminary liberation of formic acid which has subsequently undergone decomposition, $CH_2O_2 = CO_2 + H_2$. Such preliminary liberation of formic acid is attested by the fact that a very variable quantity of formic acid is found amongst the products of fermentation; and in the present instance the amount of formic acid which had thus escaped decomposition was relatively very large. It is obvious, therefore, that in computing the fermentation products, the decomposed formic acid (represented by the hydrogen + molecular equivalent of carbonic anhydride) should be added to the formic acid actually found. Adopting this plan, the fermentation products may be thus tabulated:—

C_2H_6O .... 1·2210 gram.

$C_2H_4O_2$ .... 0·3463 „

$$CH_2O_2\left\{\begin{array}{l}\text{0·3505 gram found} \ldots\ldots\ldots\ldots\ldots\ldots \\ \left.\begin{array}{ll}H_2\text{(found)}.. & \text{0·046 gram} \\ CO_2(0·046\times 22) & \text{1·012 „}\end{array}\right\}\begin{array}{l}\text{1·058 gram} \\ \text{(calculated)}\end{array}\end{array}\right\}\text{1·4085 „}$$

CO_2.... 1·1574 gram — 1·0120 = 0·1454 „

(Due to fermentation.) (Due to decomposed formic acid.)

In endeavouring to interpret these results, it must be borne in mind that the figures for carbonic anhydride must almost certainly be somewhat low, owing to a portion of the latter remaining dissolved in the liquid and thus escaping determination. The proportions in which the other products are formed are in very fair harmony with the following equation:—

$$3C_6H_{14}O_6 + H_2O = C_2H_4O_2 + 5C_2H_6O + 5CH_2O_2 + CO_2;$$

this involves the proportions—

$C_2H_4O_2$.		$5C_2H_6O$.		$5CH_2O_2$.		CO_2.
60		230		230		44
1	:	3·8	:	3·8	:	0·7

Experimental proportions—

1	:	3·5	:	4·1	:	0·4
Acetic acid.		Alcohol.		Formic acid.		Carbonic anhydride.

These proportions correspond, moreover, most strikingly with those obtained in one out of the two similar experiments made by one of us with the *Pneumococcus* of Friedländer on mannitol (Trans., 1891, **59**, 253), thus:—

1	:	3·7	:	4·1	:	0·7
Acetic acid.		Alcohol.		Formic acid.		Carbonic anhydride.

On the other hand, a second and more incomplete fermentation of mannitol with the *Pneumococcus* of Friedländer (*loc. cit.*) gave discordant results, thus:—

1	:	2·2	:	2·5	:	0
Acetic acid.		Alcohol.		Formic acid.		Carbonic anhydride.

Fermentation of Dextrose.

Two experiments made in this case were of a precisely similar nature.

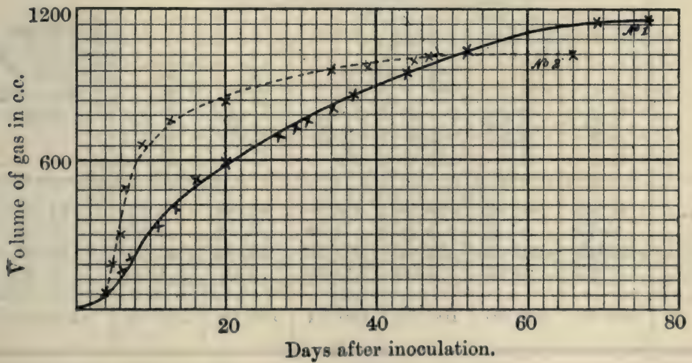
First Experiment.—430 c.c. of a 3 per cent. solution of dextrose containing also the necessary nutritive materials were fermented with a pure culture of *B. ethaceticus*, the fermentation proceeding side by side in the same incubator at 36° with that of the mannitol described above. The evolution of gas was as follows:—

No. of days after inoculation.	Volume of gas.	Total volume of gas collected.
4	Tube (1) 44·0 c.c.	44·0 c.c.
4	,, (2) 18·8 ,,	62·8 ,,
5	*,, (3) 90·0 ,,	152·8 ,,
6	,, (4) 60·0 ,,	212·8 ,,
10	*,, (5) 130·0 ,,	342·8 ,,
12	,, (6) 75·0 ,,	417·8 ,,
15	*,, (7) 102·1 ,,	519·9 ,,
19	,, (8) 66·0 ,,	585·9 ,,
26	*,, (9) 118·5 ,,	704·4 ,,
28	,, (10) 24·6 ,,	729·0 ,,
30	,, (11) 29·1 ,,	758·1 ,,
31	,, (12) 30·0 ,,	788·1 ,,
33	*,, (13) 24·0 ,,	812·1 ,,
36	,, (14) 46·0 ,,	858·1 ,,
43	,, (15) 99·0 ,,	957·1 ,,
51	,, (16) 76·0 ,,	1033·1 ,,
68	*,, (17) 106·4 ,,	1139·5 ,,
75	,, (18) 6·0 ,,	1145·5 ,,

Thus the total volume of gas collected amounted to 1145·5 c.c. as compared with 1257·0 c.c. in the fermentation of the mannitol.

We may again indicate the progress of the fermentation by means of a graphic representation in which the abscissæ show the lapse of time in days from the inauguration of the fermentation, and the ordinates the volume of gas evolved, measured in cubic centimetres:—

Fermentation of Dextrose. Nos. 1 and 2.



On comparing this curve No. 1 with that for the mannitol fermentation (p. 433), it will be seen that it is much flatter than the latter, although it is essentially of the same character as is shown by the equation which has been kindly calculated by our friend Mr. McCowan. Thus the convex portion of the curve is defined by the following equation

$$v = \frac{11t^2}{1 + 0{\cdot}197t + 0{\cdot}0068t^2},$$

in which v = volume of gas in cubic centimetres, and t = time in days from the date of inoculation.

The coincidence between calculation and observation, excepting at the extremities of the curve, where the same departures as before are noticeable, is again very close, thus :—

Day.	Volume of gas (calculated from equation).	Volume of gas (observed).
5	128 c.c.	62·8 c.c
10	301 ,,	330·0 ,,
20	574 ,,	585·0 ,,
30	759 ,,	770·0 ,,
40	890 ,,	900·0 ,,
50	988 ,,	1020·0 ,,
60	1061 ,,	1100·0 ,,

In the second fermentation of dextrose (see p. 437), the form of the curve is much more like that of the mannitol curve.

Specimens of the gas evolved at different stages of the fermentation were submitted to analysis, the particular tubes being marked * in the table on p. 437. Thus :—

Dextrose Fermentation. No. 1.

	Composition of gases evolved on						Mean excluding that of 4th—5th day.
	4th—5th day.	6th—10th day.	12th—15th day.	19th—26th day.	31st—33rd day.	51st—68th day.	
CO_2....	47·45	60·32	69·86	62·30	61·43	55·91	61·96
O......	0·10	0·11	0·10	0·08	0·13	0·55	0·19
H......	35·21	39·04	30·06	37·63	38·43	42·28	37·49
N......	17·24	0·53	0·00	0·00	0·01	1·26	0·36
	100·00	100·00	100·02	100·01	100·00	100·00	100·00

From the average composition of the evolved gas, it appears that the proportion of carbonic anhydride to hydrogen is distinctly greater than in the case of the gas given off in the fermentation of mannitol.

Assuming that the whole of the 1145·5 c.c. of gas collected had the average composition of 61·96 per cent. carbonic anhydride and 37·49 per cent. of hydrogen, there would be 710 c.c. or 1·400 gram of carbonic anhydride and 430 c.c. or 0·039 gram of hydrogen.

From the liquid, after the close of the fermentation, there were obtained, after oxidation of the alcohol, 2·115 grams of barium salt, yielding 90·97 per cent. of barium sulphate and corresponding to 0·7632 gram of ethyl alcohol; and, from the volatile acids, 2·026 grams of barium salt, yielding on analysis 94·09 and 94·19 per cent. of barium sulphate, corresponding to a mixture of 0·7191 gram of acetic acid with 0·2018 gram of formic acid.

Before summarising the results of this experiment, we would refer to the

Second Experiment, which was made under similar conditions but at quite a different time. The solution fermented contained:—dextrose, 12 grams; peptone, 0·4 gram; salt solution, 40 c.c.; calcium carbonate, 4 grams; the whole being diluted to 400 c.c. The temperature during the greater part of the fermentation was 37—38°, whilst after it was practically complete, the temperature accidentally rose above 40°; the evolution of gas took place as indicated below:—

No. of days after inoculation.	Total volume of gas collected in c.c. (corrected to 0° and 760 mm.).	
4	45·4	Temperature 37—38°.
5	187·0	
6	305·0	
7	473·6	
9	665·1	
13	755·9	
20	840·0	
34	957·0	
39	979·4	
45	1002·6	
47	1006·3	
66	1034·0	Total.

Samples of the evolved gas were, from time to time, submitted to analysis, with the following results:—

	I. 5th day.	II. 8th day.	III. 12th day.	IV. 33rd day.	V. 39th day.	Mean.
CO_2....	67·79	59·70	57·30	65·38	66·20	63·27
O......	0·10	0·08	0·14	0·40	0·02	0·15
H......	31·42	40·12	42·61	33·52	33·76	36·29
N......	0·69	0·10	0·00	0·70	0·02	0·30
	100·00	100·00	100·05	100·00	100·00	100·01

The average composition of the gas is thus almost identical with that evolved in the first experiment. Assuming that the whole of the 1034 c.c. of gas collected contained the average 36·29 per cent. hydrogen, and that the remainder was wholly composed of carbonic anhydride (thus neglecting the insignificant traces of oxygen and nitrogen found), there would be 658·8 c.c. carbonic anhydride or 1·2986 gram, and 375·2 c.c. hydrogen or 0·0336 gram.

From the liquid after the close of the fermentation, there was obtained, by oxidation of the alcohol, 1·3665 gram of barium salt, yielding 90·28 per cent. and 90·14 per cent. $BaSO_4$, corresponding to 0·493 gram of ethyl alcohol; and from the volatile acids, 1·758 gram of barium salt, yielding 93·94 per cent. and 93·92 per cent. $BaSO_4$, which corresponds to a mixture of 0·159 gram of formic acid with 0·641 gram of acetic acid. Making, again, the same calculations as described in the case of the mannitol fermentation (see p. 435), the results of these two dextrose fermentations may be summarised as follows:—

Fermentation of Dextrose.

I. (430 c.c. of 3 per cent. Dextrose Solution.)

C_2H_6O .... 0·7632 gram.

$C_2H_4O_2$.................................. 0·7191 „

$$CH_2O_2 \left\{ \begin{array}{l} 0{\cdot}2018 \text{ gram (found)} \ldots\ldots\ldots\ldots \\ H_2 \text{ (found) } 0{\cdot}039 \text{ gram} \ldots\ldots\ldots\ldots \\ CO_2\ (0{\cdot}039 \times 22)\ 0{\cdot}858 \text{ gram} \left\{ \begin{array}{l} 0{\cdot}897 \text{ gram} \\ \text{(calculated)} \end{array} \right. \end{array} \right\} \begin{array}{l} 1{\cdot}0988 \\ \text{gram.} \end{array}$$

$$CO_2 \ldots\ \underset{\text{(Due to fermentation.)}}{1{\cdot}0398 \text{ gram}} - \underset{\text{(Due to decomposed formic acid.)}}{0{\cdot}8580 \text{ gram}} = 0{\cdot}1818 \text{ gram.}$$

II. (400 c.c. of 3 per cent. Dextrose Solution.)

C_2H_6O .... 0·8375 „

$C_2H_4O_2$.................................. 0·6410 „

$$CH_2O_2 \left\{ \begin{array}{l} 0{\cdot}1600 \text{ gram (found)} \ldots\ldots\ldots\ldots \\ H_2 \text{ (found) } 0{\cdot}0336 \text{ gram} \ldots\ldots\ldots\ldots \\ CO_2\ (0{\cdot}0336 \times 22)\ 0{\cdot}7392 \text{ gram} \left\{ \begin{array}{l} 0{\cdot}7728 \text{ gram} \\ \text{(calculated)} \end{array} \right. \end{array} \right\} \begin{array}{l} 0{\cdot}9328 \\ \text{gram.} \end{array}$$

CO_2.... 0·9876 gram − 0·7392 gram = 0·2484 gram.
(Due to fermentation.) (Due to decomposed formic acid.)

We have evidence that what is recorded above as carbonic anhydride (over and above that due to decomposed formic acid) is derived from the decomposition of the calcium carbonate by an unidentified, fixed acid, insoluble in ether. For in the second of these two experiments we have determined the total calcium carbonate which passed into solution during fermentation, and found it to be 1·368 gram, corresponding to 0·6019 gram carbonic anhydride, which represents the carbonic anhydride liberated by the action of all the acids formed on the calcium carbonate. But the carbonic anhydride, due to the action of the formic and acetic acids can be calculated to be 0·3110 gram, leaving 0·2909 gram of carbonic anhydride, due to the decomposition of the calcium carbonate by the unidentified acid. This point is particularly interesting, as, if the above 0·6019 gram carbonic anhydride, due to decomposition of the calcium carbonate, be deducted from the total carbonic anhydride found by gas analysis, namely, 1·2986 gram, the remainder, 0·6967 gram of carbonic anhydride, is almost exactly what is required (viz., 0·7392 gram CO_2) to produce formic acid with the hydrogen found. The fermentation thus consists of the decomposition of the dextrose with formation of ethyl alcohol, acetic acid, formic acid (the greater part of which decomposes into carbonic anhydride and hydrogen), an unidentified fixed acid, insoluble in ether, together with traces of succinic acid, the presence of which we have found in subsequent experiments described below. The several products appear in the following molecular proportions :—

Fermentation of Dextrose.

	No. 1.		No. 2.		Molecules (mean).
	$\frac{\text{Weights}}{\text{Molecular weights}}$	Molecules.	$\frac{\text{Weights}}{\text{Molecular weights}}$	Molecules.	
C_2H_6O	0·0166	2·2	0·0182	2·8	2·5
$C_2H_4O_2$	0·0120	1·6	0·0107	1·6	1·6
CH_2O_2	0·0239	3·1	0·0203	3·1	3·1
CO_2 equivalent of unidentified acid	(0·0076)*	1	0·0066	1	1

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* As the CO_2 equivalent of the unidentified acid was not determined in this fermentation, it has been here calculated, assuming this acid to have been formed in the same proportion to the acetic and formic acids as in Fermentation No. 2.

The coincidence between the results obtained in these two fermentations, although carried on with an interval of six months between them, is very striking.

We have also carried out a number of fermentations of dextrose with *B. ethaceticus* in open flasks (plugged with cotton wool), in which, of course, the gaseous products had to be neglected. The results of these fermentations may be summarised as follows:—

No. 1.—60 grams of dextrose in 2000 c.c. of liquid were fermented. The fermentation lasted about five weeks.

By oxidation of the alcoholic portion, there were obtained—

Barium salts, 16·062 grams (yielding 91·32 per cent. $BaSO_4$), corresponding to *ethyl alcohol* 5·794 *grams.*

The volatile acids gave 11·9135 grams of barium salt (yielding 90·39 per cent. $BaSO_4$), corresponding to *acetic acid* 5·606 *grams.*

	$\frac{\text{Weights}}{\text{Molecular weights}}$	=	Molecules.
C_2H_6O	0·126		1·4
$C_2H_4O_2$	0·093		1·0

No. 2.—60 grams of dextrose in 2000 c.c. of liquid were submitted to fermentation. The fermentation lasted only about three weeks. By oxidation of the alcoholic portion there were obtained—

Barium salts 19·5315 grams (yielding 91·41 per cent. $BaSO_4$), corresponding to *ethyl alcohol* 7·047 grams.

The volatile acids gave—

Fraction I. 7·244 grams of barium salt (yielding 96·39 per cent. $BaSO_4$).

Fraction II. 3·228 grams of barium salt (yielding 95·27 per cent. $BaSO_4$).

Which corresponds to—

3·989 grams of barium formate = 1·617 *gram formic acid.*
6·483 grams of barium acetate = 3·050 *grams acetic acid.*

	$\frac{\text{Weights}}{\text{Molecular weights}}$	=	Molecules.
C_2H_6O	0·153		3·0
$C_2H_4O_2$	0·051		1·0
CH_2O_2	0·035		0·7

This is the only one of these four fermentations conducted in open flasks in which we have observed the production of any considerable proportion of formic acid; in the remaining three, formic acid was practically absent. The exceptional production of formic acid in open fermentations of mannitol has previously been observed by one of us, and is in this case not improbably connected with the unusually short duration of the fermentation.

No. 3.—30 grams of dextrose in 1000 c.c. of liquid were employed for fermentation; the fermentation lasted about 7 weeks.

By oxidation of the alcoholic portion there were obtained :—

Barium salts 8·145 grams (yielding 91·24 per cent. $BaSO_4$), corresponding to *ethyl alcohol* 2·939 grams.

The volatile acids gave—

3·488 grams of barium salts (yielding 89·70 per cent. $BaSO_4$), corresponding to 1·641 *gram of acetic acid.*

	$\frac{\text{Weights}}{\text{Molecular weights}}$	=	Molecules.
C_2H_6O	0·064		2·4
$C_2H_4O_2$	0·027		1·0

No. 4.—30 grams of dextrose in 1000 c.c. of liquid were employed for fermentation. The fermentation lasted about six weeks.

By oxidation of the alcoholic portion there were obtained—

Barium salts 7·159 grams (yielding 90·59 per cent. $BaSO_4$), corresponding to *ethyl alcohol* 2·582 *grams.*

The volatile acids gave—

5·876 grams of barium salts (yielding 91·29 per cent. $BaSO_4$), corresponding to 2·765 *grams of acetic acid.*

	$\frac{\text{Weights}}{\text{Molecular weights}}$	=	Molecules.
C_2H_6O	0·056		1·2
$C_2H_4O_2$	0·046		1·0

The results of our investigation may be summarised as follows :—

1. The principal products of the fermentation of mannitol and dextrose by *B. ethaceticus* are ethyl alcohol, acetic acid, carbonic anhydride, and hydrogen.

2. When the fermentation is conducted in a closed space, as when the gases evolved are collected over mercury, formic acid is also an invariable product, whilst in fermentations conducted in an open space (*e.g.*, flasks plugged with cotton wool), formic acid is an exceptional product. This may be accounted for by supposing that some of the carbonic anhydride and hydrogen evolved are in the first instance liberated in the shape of formic acid, and that this undergoes less complete decomposition when it is constrained to remain in contact

with its decomposition products—carbonic anhydride and hydrogen—as is the case when the fermentation is conducted in a closed space.

3. The decomposition of the mannitol may be thus represented —

$$3C_6H_{14}O_6 + H_2O = C_2H_4O_2 + 5C_2H_6O + 5CH_2O_2 + CO_2.$$

Even in the fermentations conducted in a closed space, the greater part of the formic acid in question is decomposed, whilst in open fermentations the whole generally undergoes complete resolution into carbonic anhydride and hydrogen, formic acid in any quantity being only exceptionally found amongst the products.

4. In the case of the fermentation of dextrose we have shown that there is formed, in addition to the above products, a fixed acid insoluble in ether, which we have not yet identified, but the carbonic anhydride equivalent of which we have determined.

The products of the dextrose fermentation are liberated in the following molecular proportions :—

C_2H_6O	2·5	molecules.
$C_2H_4O_2$................	1·6	„
CH_2O_2................	3·1	„
CO_2 equivalent of unidentified acid...........	1·0	„

Thus in the fermentation of dextrose the proportion of acetic acid to alcohol and formic acid is greater than in the case of the mannitol. In the case of the mannitol fermentation, it is almost certain, also, that there is a fixed acid insoluble in ether formed in addition to the products indicated, and the molecule of carbonic anhydride given in the equation above doubtless represents its equivalent, and has been obtained through the decomposition of calcium carbonate by this unidentified acid.

5. The fermentations in a closed space are always found to be very markedly less complete than those conducted under circumstances permitting of the free diffusion of the gaseous products.

6. The close qualitative and quantitative resemblance which we have established as existing between the decompositions brought about by *B. ethaceticus* and the *Pneumococcus* point to this ethacetic fermentation being a very general one which not improbably can be brought about by a number of different microorganisms.

XLI.—*Platinous Chloride and its Use as a Source of Chlorine.*

By W. A. SHENSTONE, Lecturer on Chemistry in Clifton College, and C. R. BECK.

IN a report read at the Cardiff meeting of the British Association, it was stated that chlorine obtained by the decomposition of platinous chloride had been found by one of us to contain hydrogen chloride and oxygen, together with a trace of an inactive gas, which was supposed to be nitrogen.

As platinous chloride has been described by V. and C. Meyer (*Ber.*, **12**, 1429) as easily to be obtained in a pure state, and as it has been used by them for the preparation of chlorine in some important and well known experiments, it appeared to us worth while to investigate the subject thoroughly; a more complete investigation seemed to be all the more desirable, because, soon after the meeting at Cardiff, we met with an account of some interesting experiments by M. Léon Pigeon (*Compt. rend.*, **112**, 1218), in which he described a new and apparently superior method of preparing this compound.

Before we describe our examination of the gases generated by heating platinous chloride, we wish to call attention to the following points in connection with this salt which have generally been overlooked by chemists.

1. Platinous chloride, when heated to decomposition, gives a distinct sublimate. This has previously been observed by G. Matthey (*Proc. Roy. Soc.*, **28**, 464); hence the results of analyses of this salt made by simple ignition, either in a crucible or in a current of inactive gas, cannot be depended on.

The properties of the sublimate are not always those of platinous chloride. It is sometimes a yellowish, fusible substance, converted by rather strong heat into a red, infusible solid; sometimes this red, infusible substance is obtained in the first instance.

2. If well-made platinous chloride is decomposed by heat in an exhausted tube of rather greater capacity than is necessary for the gas that will be liberated, a distinct deposit of water can usually be observed on the sides of the tube, even when the tube and salt have previously been rather strongly heated in a vacuum, and have not again been exposed to the air. This water is evidently neither attached water, nor water of crystallisation. It is far too strongly held. We have made an attempt to determine its amount in the case of a particularly good specimen of platinous chloride, prepared by the process lately described by Pigeon, of which we give a brief account later on.

0·970 gram of the salt, when heated in a current of dry air, gave 0·002429 gram of water, equal to 0·248 per cent. As the proportion of chlorine in platinous chloride is no more than 26·64 (theoretically), this quantity of water is by no means insignificant.

The determination of the water was very carefully made. The phosphoric oxide used to dry the air and to absorb the water was prepared by prolonged heating in oxygen; it was examined for chlorine at the end of the experiment, and was fully protected during the experiment from the access of any water except that from the platinum salt. The weighings were taken by the method of vibrations, and the possible effect of change of temperature was counteracted in the usual manner.

Examination of the Chlorine from Platinous Chloride.

The Material Employed.—The experiments described at Cardiff were made with platinous chloride from three distinct sources, one, a preparation made by one of us; the others, preparations from well known makers of fine chemicals. In the experiments now described we used—

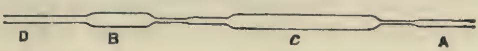
a. A specimen of platinous chloride made by ourselves from pure platinum, kindly supplied to us by Messrs. Johnson and Matthey. This salt was prepared in the usual manner by heating chloroplatinic acid in a current of dry filtered air. It was found afterwards to be practically insoluble in cold water, but to be slightly attacked by warm water.

b. A specimen prepared by heating crystals of chloroplatinic acid in an exhausted tube, together with a large excess of solid potash, the substance being successively heated to 100—200°, and then to the boiling point of mercury during many days at each temperature, as recommended by Pigeon (*loc. cit.*). This was practically insoluble both in cold and warm water.

c. A specimen of platinous chloride obtained from a well known German firm. This was readily attacked by water, both hot and cold. These preparations differed to some extent in appearance, but none of them appeared to be hygroscopic. All gave off water, as above stated, when decomposed by heat.

Method of Collecting and Analysing the Gases obtained from Platinous Chloride.—Although the volume of gas to be analysed in each case was fairly large, the proportion of some of its constituents was very small, and therefore, after the chlorine had been removed, we had to deal with residues containing several constituents, whose volume rarely exceeded 1 c.c., and frequently was far less than this. As we have attempted to analyse these small residues accurately, we give our method in some detail.

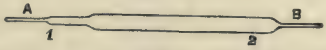
FIG. 1.



About a quarter of a gram, or rather more, of platinous chloride was introduced into the end A of the hard glass tube shown in Fig. 1. This tube was of such a capacity that it would not be quite filled by the gases from the platinous chloride used. The end A was then sealed. Phosphoric oxide was introduced into B, and the tube attached to a Sprengel pump and exhausted. As soon as the tube was well exhausted, the chamber C and the platinous chloride in A were heated somewhat strongly, the salt being heated until signs of decomposition showed themselves.

The action of the pump was afterwards continued for some time; finally the tube was sealed at D after the state of exhaustion had been measured by means of a McCleod gauge. The platinous chloride was then decomposed, the residue of platinum removed by melting off A, and the chlorine preserved in the dark for many hours.* Afterwards B, with the phosphoric oxide, was removed, and we then had a tube nearly filled with well-dried chlorine, as shown in Fig. 2, with the

FIG. 2.



ends A and B drawn out very fine, so that they might easily be broken off. A scale of equal divisions was attached to this tube from 1 to 2; its end B was thoroughly dried by warming it, and was plunged into a basin of recently distilled mercury which had been heated to 120°, and cooled in air dried by sulphuric acid. B was broken off under the mercury, and as soon as the first inrush of mercury ceased, the usual observations for finding the volume of the gas were made; the absorption of the chlorine by the mercury was then allowed to proceed and carefully observed.

The rate at which this absorption proceeds appears to be very distinctly connected with the presence or absence of moisture. It is, we believe, also conditioned by the presence of other substances, such as hydrogen chloride, and is greatly affected by the presence of diluting gases. We are investigating this subject. After the chlorine had disappeared, which can be recognised by the mercury no longer exhibiting a disposition to adhere to the glass (see p. 452), we attached the tube to the apparatus for collecting and examining the residue, shown in Fig. 3. This will almost explain itself. The tube A containing the residue to be examined was attached very securely by very thick india-rubber tube to the capillary tube B, which together with the india-rubber tube and the rest of the apparatus had been filled with mercury beforehand, the three-way tap was turned to bring B into connection with C, and the reservoir R lowered until there was a barometric vacuum in C; any air that had remained in B passed into C, and was easily expelled by way of *d*. The reservoir was then again lowered, and the vacuum maintained for some time to test the condition of the joints. We found

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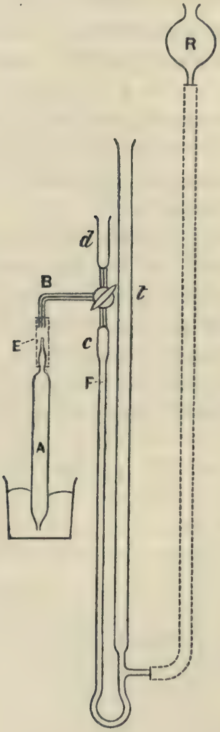
* The experiments had a twofold object. We only deal with one of these objects in this paper. For this reason the exposure of the chlorine to phosphoric oxide was of varied duration.

FIG. 3.



that when the apparatus was in proper order the leakage was exceedingly small, and we are satisfied that no appreciable error is introduced in this way during the few minutes in each analysis when the gas is under reduced pressure. This opinion is confirmed by the results of experiments that we shall have another opportunity of mentioning.

When all was right, the tip E of A was broken off, the gas in A drawn into C, and all further communication of C with the india-rubber joints was afterwards avoided.

The volume of the gas in C was next measured by expanding it to a known volume at the mark F (about 2 c.c.), and its temperature and pressure were noted. Air-free agents were afterwards introduced from D in the proper order and in very small volumes, and the volume of the residue left by each was determined. The density of the agents employed was known, and the layer of these above the mercury in C was allowed for in calculating the pressure of the gas. We believe that this method of working allowed us to analyse very small quantities of gas with considerable accuracy.

In our earlier experiments, we modified the process just described by attempting to examine the undried gases from platinous chloride. We had not then learnt that the proportion of water given off by the salt is so considerable as we afterwards found it to be. The results of these first experiments were rather unexpected. We found that the absorption of the chlorine, which, with the assistance of agitation, could be easily completed in about an hour, was followed by a secondary absorption that occupied a much longer time, and that the residue finally obtained was very much smaller than those met with by one of us at an earlier stage, when residues amounting to nearly 5 per cent. of the original gas were obtained. Thus in one analysis we had only 0·5 per cent. of residue, which was almost entirely oxygen; in another, we had a residue of 0·6 per cent., also chiefly oxygen; and a sample of chlorine prepared from salt made by Pigeon's process yielded less than 1·5 per cent. of residue when exposed to damp mercury, as compared with more than 3 per cent. when the experiment was conducted in the dry way. Part of this difference may have been due to the trace of water present dissolving some of the hydrogen chloride, but, from the slowness of the secondary absorption, it seems almost certain that it was largely in consequence of some action between one or more of the gases present and mercury, or perhaps between one or more of the gases and the products of the action of chlorine on mercury, which usually include both calomel and mercuric chloride.

These results show that when the purity of chlorine is tested by means of mercury, the results are not to be trusted unless the gas has been well dried before it is brought into contact with the mercury, and they illustrate well the kind of error that ought to be carefully watched for by those who study the chemical or physical properties of chlorine.

Having thus failed to get trustworthy results when examining the damp gas, we next proceeded to make analyses with carefully dried gas exactly in the manner described above, with the results shown in the following table. Only one analysis was made in each case, partly because each experiment takes up a very considerable period of time, and partly because the general character of the results confirms those of previous experiments and entirely settles the main question that we desired to investigate. It is worth pointing out that it is not impossible that even these final experiments, though they were conducted with great care, afford a somewhat imperfect measure of the impurity of the chlorine from platinous chloride, because we have at present no certainty that the secondary actions observed in the case of the damp gas are absent in the case of the dry gas.

No. of experiment.	Chlorine, per cent.	Hydrogen chloride, per cent.	Oxygen, per cent.	Residue, per cent.
1......	98·52	0·61	0·81	0·06
2......	97·51	1·66	0·77	0·05
3......	96·89	1·95	1·13	0·02

Experiment 1 was made with chlorine from a German preparation. In this case the salt was slightly overheated in a vacuum whilst attached to the pump.

Experiment 2 with chlorine from a preparation made by us in the usual way.

Experiment 3 with chlorine from a preparation made by Pigeon's process.

The residues given in the fifth column were only to a very small extent due to imperfect exhaustion of the tubes. They probably partly represent leakage, and afford some evidence of the absence of any serious error from this cause. They may have consisted partly of carbon monoxide, as alkaline pyrogallol was employed to absorb the oxygen.

General Conclusions.

The results of our experiments have led us to the following general conclusions :—

1. That the chlorine obtained by the decomposition of platinous chloride is usually impure, and that the impurities consist of variable proportions of hydrogen chloride and oxygen, with water and, *perhaps*, a trace of nitrogen. These impurities have been found in six specimens of chlorine, prepared from six distinct preparations of platinous chloride.

2. That platinous chloride, when prepared by any of the processes at present recommended, usually contains a small quantity of some basic compound. It is true that several observers have found that the proportion of chlorine in the salt approximates pretty closely to that required for the formula $PtCl_2$. Some of the analyses on which these statements are based were, however, made by methods which show that the volatility of the salt had been overlooked, whilst the analyses of M. Pigeon, which are not open to this objection, gave, we notice, only 99·6 of platinum and chlorine in 100 parts of the salt. If to this we add the amount of water found in our experiment, we have still only accounted for 99·85 parts in 100 parts of the salt taken.

The amounts of hydrogen chloride and oxygen found in our final exact analyses do not bear any simple or even any fixed relation to each other. This may be partly attributed to the difficulty of heating the salt exactly to the same degree in any two experiments during exhaustion and afterwards. We suspect that the hydrogen chloride is expelled before the oxygen, for we observe that in Experiment 1 the proportion of hydrogen chloride found is very low. Now, in this experiment, the preliminary heating of the salt in a vacuum was carried slightly too far; the salt was heated until the evolution of chlorine had fully commenced, instead of to a slightly lower temperature, as in the other cases. The irregularity which we notice may, however, be due partly to a secondary absorption of hydrogen chloride, such as we have already discussed in connection with the earlier experiments with damp chlorine.*

Perhaps the most important conclusion to be drawn from the experiments we have made, including many that we do not now describe, is that the preparation of chlorine, even moderately free from impurities, is a matter of far greater difficulty than has usually been supposed. It seems to us that before chlorine is employed in any research in which its purity is important, a sample of the gas to be used should be carefully examined. We call attention to this point, as the precaution in question has not, we believe, always been taken in the past. Although we have obtained chlorine more free from impurities than any specimen that we have obtained from platinous chloride, we have not yet obtained any that we can describe as pure. We hope, however, soon to supplement this paper by a communication on this subject.

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* It will be found that a salt containing platinum, chlorine, oxygen, and hydrogen, when decomposed, may not improbably give different products under different circumstances.

XLII.—*Note on the Adhesion of Mercury to Glass in the presence of Halogens.*

By W. A. Shenstone.

In my earlier experiments on the action of chlorine on mercury, my attention was very quickly called to a peculiar phenomenon which I have not hitherto seen described.

It is probably known to nearly all chemists that when clean mercury is exposed to the influence of ozonised oxygen the mercury loses its meniscus and exhibits a decided tendency to adhere to clean glass. Perhaps the prettiest method of showing this action is to deliver ozonised oxygen into a test-tube full of mercury, when, if the gas be admitted intermittently in bubbles of proper size, the mercury may be made to form thin films which adhere to the test-tube, dividing it into a series of chambers by discs of mercury. It is still a little uncertain whether this action of ozone depends on the oxidation of the mercury or not. Some experiments described to the Society by Mr. Cundall and myself, a few years ago, seemed to suggest that it is independent of any oxidising action, though by themselves the experiments are not, perhaps, quite conclusive.

When I first attempted to detect the presence of other gases in chlorine by absorbing the latter by means of mercury, I found that in the presence of chlorine, mercury acquires this power of adhering to glass in a remarkable degree, so that, if chlorine be delivered into a tube filled with mercury, the tube is entirely coated with the metal, and the presence of the gas can only be detected by the lightness of the tube. Similarly the rise and fall of the mercury in a gauge is entirely obscured by the presence of chlorine in the gas under examination. This has rather hampered Mr. Beck and myself sometimes.* On the other hand, the phenomenon has been of use, as

* It has been suggested by Dr. A. Richardson that this might be overcome by the employment of a layer of sulphuric acid above the mercury. My own experience, however, suggests that the risk of introducing sulphur dioxide into the apparatus in this way is considerable.

it has enabled us to determine with considerable exactness the point at which the absorption of chlorine by mercury from mixtures of gases becomes complete, and without its aid it is certain that we should have overlooked the peculiar secondary absorption in the presence of moisture, which we have alluded to in the preceding paper.

The action seems to occur equally well with damp and very dry chlorine.

I have thought it worth while to examine the behaviour of bromine and iodine with mercury, and I find that bromine exhibits the same phenomenon in a marked degree. The bromine employed was purified by prolonged digestion with potassium bromide, then distilled off, and placed in small bulbs. These were placed in strong glass tubes containing phosphoric oxide. The tubes were exhausted, sealed, and the bulbs of bromine were broken; after half an hour, the phosphoric oxide was removed, and one end of the tube, which now only contained bromine vapour, was attached to a reservoir containing recently distilled mercury, the tip of the tube was broken, and a little mercury admitted; the mercury was found at once to adhere to the glass quite as freely as in the presence of ozone. An essentially similar experiment was made with specimens of iodine that had been purified by Stas' method some years ago and preserved in vacuous glass bulbs, with the result that this also acts similarly, but apparently in a far less marked manner.

In all these cases the phenomena described were quickly followed by others which showed that combination had taken place.

XLIII.—*Researches on Silicon Compounds and their Derivatives. Part IV. The Action of Silicon Tetrachloride on Substituted Phenylamines.*

By J. EMERSON REYNOLDS, M.D., D.Sc., F.R.S., Professor of Chemistry, University of Dublin.

IT has been already shown, in the course of this investigation (Part V, Trans., 1889, **55**, 474), that silicon tetrabromide and tetrachloride react with aniline, orthotoluidine, paratoluidine, and α- and β-naphthylamine, producing a new class of compounds, of the form $Si(RNH)_4$.

So far only primary bases were examined, but it seemed desirable to extend the inquiry to secondary and tertiary bases, of which diphenylamine, ethylaniline, and diethylaniline seemed best suited for my immediate purpose. The results obtained with these substances are recorded in the following pages.

Silicon Tetrachloride and Diphenylamine.

17 grams of silicon tetrachloride, diluted with benzene, were added to a nearly saturated benzene solution of 140 grams of "pure" diphenylamine obtained from Kahlbaum. There was not any sensible rise in temperature on the addition of the silicon chloride, nor did any solid matter separate on standing, but the liquid assumed a dark-brown colour. The mixture did not fume when exposed to the air, as do even very dilute benzene solutions of silicon chloride; it was, therefore, evident that combination of some kind had taken place. The liquid was now gently warmed, and the benzene distilled off, almost completely, from a water-bath. The benzene distillate was found to be rich in silicon tetrachloride. This result was so unexpected, that the amount of the chloride which had volatilised was determined, and found to be 12·6 grams, or about three-fourths of the whole. The cause of the disappearance of the remaining fourth was now sought for, and for this purpose the residual liquid was mixed with four times its volume of light petroleum; the latter determined the separation of a comparatively small quantity of a brownish precipitate, which was found to contain silicon and chlorine. After the removal of this precipitate, the light petroleum was distilled off, and the solution, on cooling, became nearly solid, owing to the separation of unchanged diphenylamine.

To this was then added the first benzene distillate, rich in silicon chloride, without causing any change of colour; after digesting, as before, the benzene was distilled off, and this time carried with it *all* the silicon chloride last added, and the residue, when treated with light petroleum, did not afford any precipitate. It is, therefore, certain that the small proportion of silicon chloride which disappeared in the first instance was, in fact, used up by some impurity in the diphenylamine; but the diphenylamine purified in the first instance by silicon chloride did not retain silicon at the temperature of boiling benzene.

The contrast between the action of the silicon tetrachloride on phenylamine and on diphenylamine, is, therefore, very strongly marked. In the former case, and in presence of even relatively large proportions of diluting benzene, the following change rapidly takes place at ordinary temperatures, and is accompanied by evolution of much heat:—

$$SiCl_4 + 8PhNH_2 = Si(PhNH)_4 + 4PhNH_3Cl.$$

Diphenylamine, on the other hand, even in presence of very little benzene, only forms a very feeble addition compound with silicon tetrachloride at ordinary temperatures, and this is wholly broken up at 81°, leaving the diphenylamine intact, if pure. The effect of the substitution of one of the atoms of hydrogen in the amido-group of phenylamine by phenyl, in preventing the removal of the remaining hydrogen atom by interaction with silicon tetrachloride, is especially remarkable, in view of the facts recorded below relative to the action of the silicon haloïd on ethylphenylamine, that is, ethylaniline.

Silicon Tetrachloride and Ethylaniline.

25 grams of silicon tetrachloride, mixed with benzene, were gradually added to 145 grams (rather more than 8 mols.) of recently distilled and nearly colourless ethylaniline, previously diluted with 3 vols. of benzene. The mixture became warm, and assumed a greenish colour, which increased until about half the silicon chloride was added; it then changed to pale-brown when the mixture was complete. Very soon a granular, crystalline mass separated, which was filtered off after 24 hours. This was well washed with cold benzene, and twice recrystallised from the boiling liquid, when it was obtained pure as a felted mass of fine, colourless needles. The melting point was 172—173°.

0·1048 gram gave 0·0946 gram of AgCl = 22·32 per cent. of Cl.
Theory for $NEtPhH_2Cl$ requires 22·54 per cent. of Cl.

The compound was, therefore, ethylaniline hydrochloride. The liquid, filtered from the hydrochloride, was concentrated by distilling off some benzene, and then mixed with its own volume of light petroleum; the latter, however, only caused the separation of a small additional quantity of the hydrochloride—nearly 50 grams of which had separated up to this stage of the treatment. As the light petroleum failed to separate a silicon compound, the solvent was removed by distillation in a current of dry hydrogen, and then (since treatment with carbon bisulphide had also failed to cause crystallisation) the residue was carefully heated to 196°, in order to expel all solvents, without distilling off any material amount of the free ethylaniline which was probably present.

The residual liquid, which was brown and somewhat thick, held in solution a silicon compound and a considerable quantity of hydrochloride, the latter of which very slowly crystallised out. As all treatment with solvents had failed to separate the hydrochloride from the silicon compound, and the properties of the liquid indicated the presence of some free ethylaniline, the following plan was adopted for removing the latter, and thus simplifying the problem :—Chlorine and silicon were determined in the liquid; the percentages found were 5 95 of Cl and 2·94 of Si. On the hypothesis that the former was wholly present as ethylaniline hydrochloride, and the silicon as the supposed new compound, $Si(PhNEt)_5$, the respective percentages are 26·39 of the hydrochloride and 53·35 of the silicon compound. Assuming the residual 20·26 per cent. to consist wholly of free ethylaniline, enough silicon chloride was added to completely interact with the free base, and make it afford a further quantity of hydrochloride and of silicon compound.

The liquid was treated, as above, with the requisite quantity of silicon tetrachloride, mixed with a little benzene, and heat was evolved. As anticipated, the hydrochloride now separated out much more freely, and, after standing for 24 hours, was removed by filtration under pressure. The deep-brown filtrate was then mixed with 2 vols. more of light petroleum, which, even on standing, caused but a small amount of hydrochloride to separate, and further dilution with light petroleum had little effect. The solvents were then distilled from the filtered solution, and the residual liquid heated until there was no further loss. The residue was allowed to stand over oil of vitriol until crystallisation ceased, and the liquid portion was sealed up in a tube and set aside for several months. As no further crystals separated, the liquid was analysed, with the following results :—

1·3365 gram gave 0·1096 gram of SiO_2 = 3·824 per cent. of Si.
0·6265 gram gave 0·1645 gram of AgCl = 6·49 per cent. of Cl.

Corresponding to :—

69·95 per cent. of $Si(NEtPh)_4$.
28·60 „ „ $NEtPhH_2Cl$.

The ratio of silicon compound to hydrochloride is 1 : 1·3. All attempts to separate the constituents by solvents gave negative results, and fractional distillation in a vacuum led to decomposition. Whether the material is a liquid compound of the hydrochloride and silicon tetraphenylethylamide or a solution of the hydrochloride in the silicon compound, there is no doubt that the latter is formed by the interaction of silicon tetrachloride and ethylaniline. Hence the substitution of ethyl for hydrogen in aniline does not interfere with the general course of the interaction with silicon tetrachloride; while the exchange of phenyl for hydrogen in aniline prevents such interaction altogether, as shown in the case of diphenylamine.

Silicon Tetrachloride and Diethylaniline.

25 grams of silicon tetrachloride, diluted with benzene, were added to 175 grams of recently distilled diethylaniline boiling at 213—214°, also diluted with rather less than an equal volume of benzene. The temperature of the mixture rose a few degrees and the colour changed from pale yellow to brown; after standing for half an hour, crystalline plates separated, but in comparatively small quantity.

The mixture was then heated at 90° under slight pressure for eight hours without materially increasing the amount of the crystals, and was subsequently distilled until a volume of distillate was obtained greater than that of the benzene used. The distillate fumed strongly and evidently contained a silicon compound; this proved to be unchanged silicon tetrachloride, 22·5 grams of which were present in the distilled liquid. Hence only 2·45 grams had reacted with the diethylaniline. The residual, brown liquid from which benzene and silicon chloride had been removed did not fume on exposure to air, and, on cooling, gave a small crop of the crystals already mentioned; the latter were collected and recrystallised from benzene. They did not contain silicon:—

0·2162 gram gave 0·1665 gram of AgCl = 19·04 per cent. Cl.

Theory for $C_6H_5 \cdot NEt_2HCl$ requires 19·13 per cent. of Cl.

The liquid filtered from the crystals of hydrochloride was then distilled; a few drops came over below 200°, but the temperature quickly rose to 213—214°, at which unchanged diethylaniline was obtained, accompanied by a small amount of hydrochloride, which partially volatilised with the vapour of the free base and even with benzene; when but a small residue was left, decomposition began and the operation was stopped. This residue, when cold, was a pasty mixture of hydrochloride and a silicon compound, but the quantity of the latter was too small for satisfactory separation, as solvents did not completely remove unchanged hydrochloride from it.

An attempt was made to increase the interaction in the following way:—17·5 grams of pure diethylaniline and 2·5 grams of silicon chloride were mixed in a pressure tube and the latter sealed. Crystals separated as when benzene was used. The contents of the tube were then gradually heated to 140° and kept at that temperature for an hour, but no marked change occurred, and the temperature was raised to 190° for half an hour. A brown liquid resulted, and crystals of the hydrochloride separated on cooling; but not in greater proportion than in the first experiment. When the tube was opened, *no trace of ethyl chloride* could be detected, but unchanged silicon chloride was easily distilled off, and, subsequently, diethylaniline, leaving a small siliceous residue.

Hence diethylaniline and silicon tetrachloride interact to a very small extent even at 190°, and the NEt_2 group is not attacked, since ethyl chloride is not separated.

On the other hand, the formation of the small amount of diethylaniline hydrochloride obtained involves the removal of some hydrogen from the phenyl residue; hence it is probable that the pasty siliceous mixture left after removal of excess of silicon chloride and diethylaniline contained the compound $Si(C_6H_4{\cdot}NEt_2)_4$.

Therefore, the substitution of phenyl for but 1 atom of hydrogen in aniline confers on the resulting base greater immunity from attack by silicon tetrachloride than replacement by ethyl of part or all the amidic hydrogen of aniline.

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XLIV.—CONTRIBUTIONS FROM THE LABORATORIES OF THE HERIOT WATT COLLEGE.

Action of Nitric Acid on Oxanilide and Similarly Constituted Substances.

By A. G. Perkin.

The nitro-derivatives of the aromatic amines such as nitraniline, &c., are usually prepared either by the direct action of nitric acid on the amines themselves, or on their acetyl compounds, the latter method being most generally employed. In this way one nitro-group may be readily introduced into the amine, but subsequent nitration of the mononitro-derivative can only with difficulty be accomplished. Thus metadinitraniline may be prepared by the hydrolysis of dinitracetanilide, but as the latter is difficult to obtain in any quantity, other methods of preparation have from time to time been proposed, as for instance, heating α-chlorometadinitrobenzene with alcoholic ammonia, &c., but all these methods are difficult to carry out on any scale.

Trinitraniline, on the other hand, has not been obtained direct from aniline or its derivatives, and the method employed in preparing it is so tedious that it is difficult to obtain in any quantity. These considerations led me to undertake experiments with the object of preparing these substances and their homologues readily and in quantity. During the course of the experiments, I noticed that oxanilide, when treated with nitric acid, is converted not only into dinitroxanilide, $(CO\cdot NH\cdot C_6H_4\cdot NO_2)_2$, but also quite readily and almost quantitatively into tetranitroxanilide, $[CO\cdot NH\cdot C_6H_3(NO_2)_2]_2$, and into hexanitroxanilide, $[CO\cdot NH\cdot C_6H_2(NO_2)_3]_2$, according to the conditions employed.

These derivatives, on hydrolysis, yield the corresponding nitranilines, thus—

$$[CO\cdot NH\cdot C_6H_3(NO_2)_2]_2 + 2H_2O = 2C_6H_3(NO_2)_2NH_2 + C_2H_2O_4,$$

and

$$[CO\cdot NH\cdot C_6H_2(NO_2)_3]_2 + 2H_2O = 2C_6H_2(NO_2)_3\cdot NH_2 + C_2H_2O_4.$$

Similarly, on nitrating ortho- and para-oxalotoluidides, tetranitro-derivatives of these compounds are obtained, the yield in these cases also being nearly quantitative; hexanitro-ortho- and para-oxalotoluidides, however, could not be prepared by these methods. On hydrolysis these tetranitro-derivatives yielded the corresponding dinitrotoluidines.

The results obtained in the study of the action of nitric acid on the oxalyl derivatives of α- and β-naphthylamine were not so satisfactory, for it was found that although dinitro-derivatives could be readily obtained, yet, owing to the less stable nature of these compounds, they were decomposed on further treatment into tetranitro-derivatives of the corresponding carbamides.

Thus, oxalo-β-naphthylide, on treatment with nitric acid, yields, in the first place, dinitroxalo-β-naphthylide, $(CO\cdot NH\cdot C_{10}H_6\cdot NO_2)_2$, and then tetranitro-$\beta$-dinaphthylcarbamide, $CO\cdot[NH\cdot C_{10}H_5(NO_2)_2]_2$.

It seems probable that the nitration of the oxalyl compounds of other amines, with the study of which I am still engaged, may prove a ready means of obtaining nitramines, which can otherwise only be prepared with difficulty.

Preparation of Oxanilide and its Homologues.

During the course of these experiments, it was thought desirable to find a means of preparing these compounds rapidly and in a state of purity, and for this purpose it was necessary to obtain some high boiling liquid which would form a solvent both for the amines themselves and also for the oxalyl compounds of the same. The best solvent for this purpose was found to be that portion of the so-called coal tar "cresylic acid" which boils below 200°, consisting chiefly of a mixture of the cresols.

To prepare the oxalyl compound, the oxalate of the amine was added to the boiling cresylic acid as long as it dissolved, and then boiled for a few minutes. On cooling, crystals of the pure oxalyl compound separated, and were collected upon a cloth or gauze filter and washed with benzene.

An analysis of oxaloparatoluidide prepared in this way gave the following result:

0·1639 gram gave 14·9 c.c. N; $t = 17°$; bar. = 750 mm.

	Theory for $(CO{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3)_2$.	Found.
N	10·44 per cent.	10·40 per cent.

As would be expected by the use of such a high boiling solvent, the oxalyl compounds are obtained by this method in crystals of large size and much beauty, and the whole operation can be performed in a very short time.

Tetranitroxanilide, $C_{14}H_8N_6O_{10} = [CONH{\cdot}C_6H_3(NO_2)_2]_2$ $[NH : NO_2 : NO_2 = 1 : 2 : 4]$.

When finely-powdered oxanilide is added to nitric acid of sp. gr. 1·5, it is energetically attacked and dissolved, forming in the first instance a clear solution, but on adding more, crystals of the dinitro-compound separate, and after a short time the whole sets to a thick, creamy mass. On heating the product with the addition of sufficient acid to form a clear solution, and then slowly distilling off the acid, colourless needles gradually separate. These are collected on a glass wool filter, washed with nitric acid, then with glacial acetic acid, and dried. By evaporating the acid filtrate a further quantity of the tetranitroxanilide may be obtained.

On analysis, the substance, dried at 100°, gave the following numbers:—

0·2060 gram gave 35 c.c. N.; $t = 13°$; bar. = 745 mm.

	Theory for $[CONH{\cdot}C_6H_3(NO_2)_2]_2$.	Found.
N	20·0 per cent.	19·67 per cent.

The substance, which is pure tetranitroxanilide, is obtained by this method as a colourless, glistening mass of needles. By crystallisation from a large excess of fuming nitric acid these can be obtained an inch and more in length. It is insoluble in most of the usual solvents, and but moderately soluble in nitrobenzene and phenol; a mixture of fuming nitric and acetic acids is a good solvent for it. It does not melt below 270°, but when heated in a test tube it melts to a brownish liquid, which, at a slightly higher temperature, is suddenly decomposed, forming a cloud of black vapour. Hot aniline dissolves it, forming a yellow solution, which, on cooling, deposits reddish-orange plates of an aniline compound mixed with colourless needles of the original substance, but these compounds could not be readily separated from one another.

Tetranitroxanilide can also be prepared by the action of a well-cooled mixture of nitric acid (sp. gr. 1·5, 2 parts) and sulphuric acid (1 part) on oxanilide, and pouring the product into water.

The yield obtained by the first method is theoretical, 1 gram of oxanilide yielding 1·749 grams of tetranitroxanilide; theory requiring 1·75 grams.

Hydrolysis of Tetranitroxanilide.—Tetranitroxanilide does not dissolve in cold concentrated sulphuric acid, but on heating the mixture to 160—165°, it slowly dissolves with evolution of gas and formation of an orange-coloured solution. On pouring this into water, yellow flocks are precipitated; this precipitate, when collected, washed with water, and dried at 100°, crystallises from glacial acetic acid in plates which melt at 175°. On analysis, the following numbers were obtained:—

0·1905 gram gave 37·8 c.c. N; $t = 14°$; bar. $= 745$ mm.

	Theory for $C_6H_3(NO_2)_2 \cdot NH_2$.	Found.
N	22·95 per cent.	22·82 per cent.

The substance is, therefore, dinitraniline [$NH_2 : NO_2 : NO_2 = 1 : 2 : 4$].

Prepared in this way, dinitraniline is obtained at once in a pure state, one crystallisation being sufficient to render it pure enough for analysis. The yield is as follows:—

0·2 gram of tetranitroxanilide gave 0·1425 gram of crude dinitraniline, or 82 per cent. of the theoretical. Theory requires 0·174 gram.

Potash solution dissolves tetranitroxanilide only very sparingly in the cold, forming an orange-coloured solution, but, on heating, it dissolves very readily, forming a deep-red solution, which, on boiling, gradually deposits yellow crystals. On cooling, the liquid becomes filled with these. After crystallisation from glacial acetic acid, they are obtained as yellow plates, which melt at 175° and have all the properties of metadinitraniline. The dinitraniline is pure, and the yield by this method is as follows:—

1 gram of tetranitroxanilide gave 0·714 gram of dinitraniline. Theory requires 0·8714 gram. Yield = 81·59 per cent.

Hexanitroxanilide, $C_{14}H_6N_8O_{14} = [CO{\cdot}NH{\cdot}C_6H_2(NO_2)_3]_2$
$[NH : NO_2 : NO_2 : NO_2 = 1 : 2 : 4 : 6]$.

When tetranitroxanilide is added to a mixture of sulphuric acid and nitric acid (sp. gr. 1·5), it does not dissolve, and no action takes place. On warming gradually to the boiling point, however, a change occurs. The needles, without apparently going into solution, suddenly become transformed into minute plates, and the mixture assumes a satiny appearance. The product is poured into a large bulk of water, and the crystalline mass collected, washed with water, and dried.

On analysis, the following numbers were obtained :—

0·1243 gram gave 23·3 c.c. N; $t = 14°$; bar. = 754 mm.
0·1628 „ 0·1995 gram CO_2 and 0·0259 gram H_2O.

	Theory for $[CO{\cdot}NH{\cdot}C_6H_2(NO_2)_3]_2$.	Found. I.	Found. II.
C........	32·94 p. c.	—	33·41 p. c.
H........	1·17 „	—	1·44 „
N........	21·96 „	21·87	— „

This same substance can also be readily prepared by acting on oxanilide with a boiling mixture of fuming nitric and sulphuric acids. Hexanitroxanilide forms a beautiful, satiny mass of minute, thin plates. It dissolves in fuming nitric acid to a much less extent than the tetranitro-compound, and is only moderately soluble in phenol and nitrobenzene. Heated in a capillary tube, it darkens at 220° and fuses with decomposition between 255° and 260°.

Hexanitroxanilide is distinguished by its great stability towards mixtures of fuming nitric and sulphuric acids even at elevated temperatures. After being heated in a sealed tube with these acids at 170° for three hours, it was practically unaltered, and in another experiment, when heated under similar conditions at 210° for one hour, it had been but slightly attacked.

The yield from the tetranitro-compound, if the reaction is carefully carried out, is nearly theoretical, thus :—

1 gram of tetranitroxanilide gave 1·1705 grams of hexanitroxanilide. Theory, 1·214 grams.

From oxanilide the yield is also good :—

1 gram of oxanilide gave 2·01 grams of hexanitroxanilide. Theory, 2·1 grams.

Hydrolysis of Hexanitroxanilide.—Hexanitroxanilide is insoluble in cold sulphuric acid, but at a temperature of 170—180° it gradually dissolves with evolution of gas, forming an orange-coloured solution, which deposits yellow flocks on pouring into water. These were collected, washed, and dried, and crystallised from glacial acetic acid. The substance thus obtained crystallised in orange plates having a steel-blue reflex, melted at 188°, and showed all the properties of trinitraniline.

On analysis, the following numbers were obtained :—

0·1437 gram gave 29·8 c.c. N ; $t = 15°$; bar. = 764 mm.

	Theory for $C_6H_2(NO_2)_3{\cdot}NH_2$.	Found.
N	24·56 per cent.	24·42 per cent.

The amount obtained from 0·2 gram of hexanitroxanilide was 0·1380 gram or 69 per cent. In another experiment, 1·16 grams of hexanitroxanilide gave 0·78 gram or 69 per cent. Theory requires 89·41 per cent.

The yield found is, therefore, practically 80 per cent. of that required by theory, so that the yield of trinitraniline from aniline would be 200 per cent. by weight.

The action of alkalis on hexanitroxanilide is not similar to the action on the tetranitro-compound, as no trinitraniline is obtained. It dissolves very sparingly in cold aqueous alkali, more readily so on boiling, with the formation of an orange-coloured solution. This solution was acidified, a slight quantity of suspended matter filtered off, and the filtrate extracted with ether. The ethereal solution, on evaporation, deposited a gelatinous mass of yellow needles, which were obtained in a colourless condition on recrystallisation from alcohol.

I am at present engaged with the investigation of this substance.

Dinitroxalorthotoluidide, $C_{16}H_{14}{\cdot}N_4O_6 = (CO{\cdot}NH{\cdot}C_6H_3(NO_2){\cdot}CH_3)_2$
$[CH_3 : NH_2 : NO_2 = 1 : 2 : 5]$.

When oxalorthotoluidide is added to a boiling mixture of glacial acetic acid (2 parts) and nitric acid (sp. gr. 1·5, 1 part), it dissolves, forming a colourless solution, which, on cooling, deposits crystals, which are collected and purified by crystallisation from phenol.

On analysis, the following numbers were obtained :—

0·1490 gram gave 20·1 c.c. N. ; $t = 13°$; bar. = 745 mm.

	Theory for $\begin{matrix}CO{\cdot}NH{\cdot}C_6H_3(NO_2){\cdot}CH_3\\CO{\cdot}NH{\cdot}C_6H_3(NO_2){\cdot}CH_3\end{matrix}$.	Found.
N	15·64 per cent.	15·62 per cent.

Dinitroxalorthotoluidide forms long, colourless, flat needles, which melt above 260°, and can be sublimed with partial decomposition.

When heated with concentrated sulphuric acid, it dissolves, and on pouring it into water, an almost colourless solution is obtained. On adding ammonia to the hot solution and cooling, beautiful yellow plates of nitrotoluidine are deposited, which, after recrystallisation from water, melt at 130°.

Tetranitroxalorthotoluidide, $C_{16}H_{12}N_6O_{10} = [CO{\cdot}NH{\cdot}C_6H_2(NO_2)_2{\cdot}CH_3]_2$
$[CH_3 : NH : NO_2 : NO_2 = 1 : 2 : 3 : 5]$.

This is prepared by dissolving oxalorthotoluidide in nitric acid of sp. gr. 1·5, and boiling the solution for a short time. If the hot product is carefully diluted with water until crystals begin to separate, and then allowed to cool, a pasty mass is obtained, consisting of minute, colourless needles. These, after being collected and washed with water, are dried and purified by crystallisation from phenol.

On analysis, the following numbers were obtained:—

0·1575 gram gave 25·8 c.c. N; $t = 15°$; bar. = 744 mm.

	Theory for $CONH{\cdot}C_6H_2(NO_2)_2{\cdot}CH_3$ $CONH{\cdot}C_6H_2(NO_2)_2{\cdot}CH_3$	Found.
N	18·74 per cent.	18·77 per cent.

Tetranitroxalorthotoluidide does not melt below 270°, and is almost insoluble in the ordinary solvents. It is much more soluble in fuming nitric acid than the corresponding aniline compound.

On heating with concentrated sulphuric acid at 170°, a brownish-yellow solution is formed which, on dilution with water, extraction with ether, &c., yields dinitrotoluidine; this, after recrystallisation from glacial acetic acid, is obtained in long, orange-yellow plates melting at 209°.

By boiling with a mixture of sulphuric and nitric acids, oxalorthotoluidide does not appear to give a hexanitro-compound, and tetranitroxalorthotoluide is not altered by similar treatment, as appears from the following analysis of the regenerated product:—

0·1320 gram gave 20·8 c.c. N.; $t = 9°$; bar. = 736 mm.

	Theory for $CO{\cdot}NH{\cdot}C_6H_2(NO_2)_2{\cdot}CH_3$ $CO{\cdot}NH{\cdot}C_6H_2(NO_2)_2{\cdot}CH_3$	Found.
N	18·74 per cent.	18·34 per cent.

Long boiling with a mixture of these acids produces decomposition, the product, on pouring into water, dissolving, forming a clear, yellow solution.

Tetranitroxalparatoluidide, $C_{16}H_{12}N_6O_{10} = [CO{\cdot}NH{\cdot}C_6H_2(NO_2)_2{\cdot}CH_3]_2$
$[CH_3 : NO_2 : NH_2 : NO_2 = 1 : 3 : 4 : 5]$.

Oxalparatoluidide, on treatment with nitric acid (sp. gr. 1·5), behaves in a very similar manner to oxanilide. The product of the reaction, after being washed with acetic acid and dried, consists of small, colourless needles which do not melt below 270°, but become brown at that temperature. It is practically insoluble in all the usual solvents, moderately soluble in nitrobenzene, from which it crystallises in microscopic needles; it is also only very slightly soluble in acetic anhydride. Its solubility in fuming nitric acid is intermediate between that of tetranitroxanilide and tetranitroxalorthotoluidide.

On analysis, the following numbers were obtained :—

0·1900 gram gave 31 c.c. N ; $t = 15°$; bar. = 745 mm.

	Theory for $\begin{matrix}CO{\cdot}NH{\cdot}C_6H_2(NO_2)_2{\cdot}CH_3\\CO{\cdot}NH{\cdot}C_6H_2(NO_2)_2{\cdot}CH_3\end{matrix}$.	Found.
N	18·74 per cent.	18·73 per cent.

When boiled with a strong aqueous solution of caustic potash, it does not appear to dissolve, but the liquid becomes filled with bright, scarlet needles which evidently consist of a potassium compound. This, on treatment with acid, is reconverted into tetranitroxalparatoluidide.

When heated with concentrated sulphuric acid at 170°, it dissolves with evolution of gas, and on pouring into water, extracting with ether, &c., dinitroparatoluidine is obtained in orange-yellow plates, which after purification by crystallisation from alcohol, melt at 164—166°.

In order to determine whether oxalparatoluidide would yield a higher nitrated derivative, a small quantity of the tetranitro-compound was treated with a mixture of 3 parts of sulphuric acid and 2 parts of nitric acid (1·5), and the whole boiled for about 20 minutes. A small quantity of water was added to the hot mixture, which was then set aside to cool; crystals gradually separated, and the whole soon set to a semi-solid, glistening mass. The crystals were collected, washed with glacial acetic acid, and dried, and the product, which then appeared as a colourless, crystalline mass, having a beautiful silvery lustre, was analysed with the following result :—

0·1220 gram gave 19·05 c.c. N ; $t = 14°$; bar. = 736 mm.
0·1315 „ 20·2 c.c. N ; $t = 13°$; bar. = 736 mm.

	Theory for $\begin{matrix}CONH{\cdot}C_6H_2(NO_2)_2{\cdot}CH_3\\CONH{\cdot}C_6H_2(NO_2)_2{\cdot}CH_3\end{matrix}$.	Found.	
		I.	II.
N	18·74 p. c.	17·73	17·57 p.c.

As the percentage of nitrogen it contains is lower than that required by tetranitroxalparatoluidide, it is evident that the reaction is not analogous to the action of nitric and sulphuric acids on oxanilide, oxidation, and not further nitration, having taken place.

This substance, when heated in a capillary tube, becomes brown at 214°, and suddenly melts with decomposition at about 250°. Hot aqueous caustic alkalis dissolve it, and from the red solution formed acids throw down a white, crystalline precipitate, which can be recrystallised from alcohol, in which it is very soluble. I am at present engaged with the further investigation of this reaction.

Dinitroxal-β-naphthalide, $C_{22}H_{14}N_4O_6 = [CO{\cdot}NH{\cdot}C_{10}H_6NO_2]_2$
$[NO_2 : NH = \alpha : \beta]$.

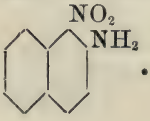
On adding oxalo-β-naphthalide to a mixture of 2 parts of glacial acetic acid and nitric acid (sp. gr. 1·5), and boiling for a short time, the solution gradually deposits a light, yellow, flocculent substance. When this is crystallised from hot nitrobenzene, a mixture of long, flat, microscopic needles is obtained, with a small quantity of opaque nodules. To separate these, the product is dissolved in boiling nitrobenzene, and the solution allowed to cool until some crystals have been deposited. The whole is then thrown on to a glass wool funnel, and the residue washed with nitrobenzene and recrystallised from the same solvent. On treating the deposit from the cooled filtrate in a similar manner, more of this substance may obtained.

Analysis gave the following numbers :—

0·1725 gram gave 19·1 c.c. N; $t = 14°$; bar. = 760 mm.

	Theory for $\begin{matrix} CO{\cdot}NH{\cdot}C_{10}H_6{\cdot}NO_2 \\ CO{\cdot}NH{\cdot}C_{10}H_6{\cdot}NO_2 \end{matrix}$.	Found.
N	13·02 per cent.	13·02 per cent.

Prepared in this manner, dinitroxal-β-naphthalide consists of yellow plates having a beautiful, golden lustre, it does not melt below 270°, but at higher temperatures is decomposed, giving off a cloud of yellow vapour. Nitrobenzene is the best crystallising agent for this substance, it being only very slightly soluble in the usual lower boiling solvents. Hot alcoholic potash dissolves it readily, forming a yellow solution which, after treatment with acid, deposits orange-red needles on cooling. These, after recrystallisation from dilute alcohol, melt at 126—127°, and have all the properties of α-nitro-β-naphthylamine,



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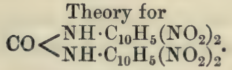
Tetranitro-β-dinaphthylcarbamide, $C_{21}H_{12}N_6O_9 = CO[NH\cdot C_{10}H_5(NO_2)_2]_2$.

On boiling dinitroxal-β-naphthalide with nitric acid of sp. gr. 1·5 purified by boiling with nitrate of urea, it dissolves, and after distilling off a portion of the nitric acid from the solution, a light, orange-coloured, crystalline powder is gradually deposited. After cooling, glacial acetic acid is added, the whole filtered, and the residue washed with acetic acid and dried.

On analysis, the following numbers were obtained:—

0·1730 gram gave 27·3 c.c. N; $t = 14°$; bar. = 720 mm.

	Theory for  $CO{<}\begin{matrix}NH\cdot C_{10}H_5(NO_2)_2\\NH\cdot C_{10}H_5(NO_2)_2\end{matrix}$.	Found.
N	17·07 per cent.	17·51 per cent.

This substance, which is probably tetranitrodinaphthylcarbamide, is a yellow, crystalline powder, consisting of small, hexagonal, microscopic plates. At a high temperature, it decomposes before melting with a slight explosion and emission of black vapour. It is almost insoluble even in solvents of high boiling point, and attempts to recrystallise it have, up to the present, been unsuccessful. Sulphuric acid does not dissolve it in the cold, and only with difficulty at high temperatures, forming a brown solution, which dissolves completely in water.

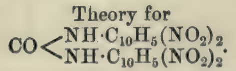
It is almost insoluble in cold aqueous solutions of the alkalis, but on warming dissolves readily, forming a scarlet solution; this becomes brown on boiling, and on adding an acid, a dirty brown-red precipitate is thrown down.

Experiments are in progress with the hope of proving more definitely the constitution of this substance.

Tetranitro-α-dinaphthylcarbamide, $C_{21}H_{12}N_6O_9 =$
$CO[NH\cdot C_{10}H_5(NO_2)_2]_2$.

Oxal-α-naphthalide is attacked by nitric acid (sp. gr. 1·5) in a similar way to the β-compound. Boiled with this acid, it dissolves, and after a short time a yellow, crystalline powder begins to be deposited; this, after washing with acetic acid and drying at 100°, gave the following numbers:—

0·1710 gram gave 25·7 c.c. N; $t = 13°$; bar. = 750 mm.

	Theory for  $CO{<}\begin{matrix}NH\cdot C_{10}H_5(NO_2)_2\\NH\cdot C_{10}H_5(NO_2)_2\end{matrix}$.	Found.
N	17·07 per cent.	17·52 per cent.

Tetranitro-α-dinaphthylcarbamide closely resembles the corresponding β-naphthyl compound in all its properties. It is a yellow, crystalline powder melting above 300° and insoluble in almost all solvents. A substance evidently identical with the above is obtained by the action of nitric acid on α-dinaphthylguanidine in the presence of ether.

Tetranitro-α-naphthylcarbamide dissolves in ammonia and the alkalis, slightly in the cold, more readily on warming, forming an orange-coloured solution, from which acids throw down a gelatinous, orange-red precipitate; this, on further heating, becomes darker in colour, passing finally into a dirty brown. Tetranitro-α-naphthylcarbamide is insoluble in cold sulphuric acid, but on warming, it dissolves sparingly with evolution of gas and formation of a dark-brown solution; on pouring this into water, it deposits dark-brownish flocks, from which nothing definite could be isolated.

Mononitroxanilic Acid, $C_8H_6N_2O_5 = C_6H_4(NO_2)\cdot NH\cdot CO\cdot COOH$ $[NH : NO_2 = 1 : 4]$.

This acid is best prepared by adding oxanilic acid to well-cooled nitric acid (sp. gr. 1·5), which has been purified with nitrate of urea. I dissolves quietly in the acid, and after some quantity has been added, needles commence to separate, and the whole soon sets to a solid mass. A little water is then added, the product collected, washed with water, and recrystallised from this solvent.

An analysis of the substance dried at 100° gave the following numbers:—

0·1493 gram gave 17·2 c.c. N; $t = 10°$; bar. = 740 mm.

	Theory for $C_6H_4NO_2\cdot NH\cdot CO\cdot COOH$.	Found.
N	13·33 per cent.	13·43 per cent.

Thus prepared, it consists of colourless, silky needles, and is identical with the paranitroxanilic acid prepared by Aschan (*Ber.*, **18**, 2936).

Dinitroxanilic Acid, $C_8H_5\cdot N_3O_7 = C_6H_3(NO_2)_2\cdot NH\cdot CO\cdot COOH$ $[NH : NO_2 : NO_2 = 1 : 2 : 4]$.

In order to prepare this substance, oxanilic acid is added to a large excess of nitric acid (sp. gr. 1·5) and the solution boiled until red fumes cease to be given off. It is then diluted with about one-third of its bulk of water, and the hot solution set aside to cool. Crystals gradually appear, and, after standing for about an hour, the separation is complete. The substance was collected, washed with water, and dried at 100°.

On analysis, the following numbers were obtained :—

0·1503 gram gave 21·4 c.c. N ; $t = 13°$; bar. = 738 mm.

	Theory for $C_6H_3(NO_2)_2NH{\cdot}CO{\cdot}COOH$.	Found.
N	16·47 per cent.	16·25 per cent.

Dinitroxanilic acid crystallises in almost colourless plates, which melt with decomposition at 176—178°. Strongly heated, it decomposes with a slight explosion. It is sparingly soluble in water, more readily so in alcohol and acetic acid.

The ammonium salt, which is best prepared by adding ammonia to a warm alcoholic solution of the acid, crystallises in thin plates, almost insoluble in alcohol, and but sparingly soluble in hot water. The barium salt is obtained as a white precipitate, insoluble in water, on treating a solution of the ammonium salt with barium chloride. The salts of the heavy metals are mostly insoluble in water, and may be obtained in the same manner from the ammonium salt. Dilute caustic soda throws down from an alcoholic solution of the acid an orange-red, gelatinous precipitate, which is very soluble in water.

On boiling an aqueous solution of dinitroxanilic acid with a little aqueous potash, yellow crystals soon commence to separate from the solution, and these, after being collected and crystallised from glacial acetic acid, appear as orange plates melting at 175°, and having all the properties of metadinitraniline. Thus prepared, this substance is exceedingly pure, and the yield obtained is almost quantitative.

Cold concentrated sulphuric acid dissolves dinitroxanilic acid, forming an almost colourless solution which, on heating to 170°, becomes slightly yellower and evolves gas. Water added to this solution precipitates yellow flocks, consisting of metadinitraniline.

Trinitroxanilic Acid, $C_8H_4N_4O_9 = C_6H_2(NO_2)_3{\cdot}NH{\cdot}CO{\cdot}COOH$ $[NH : NO_2 : NO_2 : NO_2 = 1 : 2 : 4 : 6]$.

In order to prepare this substance, oxanilic acid is boiled with a mixture of 2 parts of nitric acid of sp. gr. 1·5 and 1 part of sulphuric acid. The solution, after carefully diluting with one half its volume of water and allowing to cool, sets to a crystalline mass, which is collected and washed with water.

On analysis, the following numbers were obtained :—

0·1875 gram gave 30·1 c.c. N ; $t = 13°$; bar. = 742 mm.

	Theory for $C_6H_2(NO_2)_3{\cdot}NH{\cdot}CO{\cdot}COOH$.	Found.
N	18·66 per cent.	18·52 per cent.

Trinitroxanilic acid forms colourless needles which, at about 220°, melt with decomposition to a brown liquid. Strongly heated in a test-tube, it decomposes with a slight explosion. It is moderately soluble in alcohol, but only sparingly in water.

The ammonium salt, which is best prepared by adding ammonia to a concentrated alcoholic solution of the acid, crystallises in almost colourless, long, narrow plates, more soluble in water and alcohol than the corresponding salt of dinitroxanilic acid. Solutions of this salt in water give precipitates with salts of copper and lead. The barium salt of trinitroxanilic acid is soluble in water and crystallises in needles.

Concentrated sulphuric acid does not appear to dissolve it in the cold, but does so at a temperature of about 60°, forming a colourless solution, which, at 160°, becomes darker and evolves gas; on pouring into water, a light-yellow solution is obtained, and no trinitraniline separates.

On boiling an alkaline solution of the sodium or potassium salt of trinitroxanilic acid, beautiful, glittering, yellow crystals gradually separate; these, after filtration, can be crystallised from glacial acetic acid. The product melts at 188°, and has all the properties of trinitraniline. Prepared in this way, trinitraniline is obtained in a chemically pure condition, and without crystallisation from glacial acetic acid. The yield obtained is nearly quantitative.

In conjunction with Mr. J. E. Mackensie, I am continuing the investigation of these interesting substances.

XLV.—CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Existence of two Crystalline Acetaldoximes.

By WYNDHAM R. DUNSTAN and T. S. DYMOND.

(First Notice.)

IN July of last year we prepared a considerable quantity of acetaldoxime by the method suggested by Victor Meyer (*Ber.*, **15**, 1526), in which aldehyde is caused to react with an aqueous solution of hydroxylamine hydrochloride mixed with the calculated quantity of sodium hydroxide, $CH_3{\cdot}CHO + NH_2{\cdot}OH = H_2O + CH_3{\cdot}CH{:}N{\cdot}OH$. The mixture was extracted with ether, the solution dried with calcium chloride, and the ether carefully distilled off. The residual liquid, after being purified by distillation, finally boiled constantly at 114·5° (corr.). The properties of the compound agreed with those recorded by Petraczek (*Ber.*, **15**, 2784). To our surprise the liquid soon solidified to a mass of acicular crystals; some days subsequently their melting point was ascertained to be 37°, but on further standing it had risen to 46·5° (corr.), at which it remained constant. Acetaldoxime has hitherto been regarded as a liquid, and, indeed, we had previously kept other specimens for several days at a temperature of 10—20° without solidification taking place. To make sure that the crystalline compound was actually acetaldoxime, the crystals were quickly melted by surrounding the vessel containing them with hot water, and the boiling point of the substance again determined. It still boiled constantly at 114·5°, and there could, therefore, be no doubt as to the identity of the crystals.

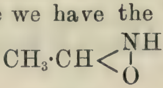
The freezing point of this liquid, which had just been heated to its boiling point, was then ascertained, and we were astonished to find that this apparently pure substance, which, a short time before, had melted at 46·5°, now refused to crystallise at 20° even after a crystal of the original substance (m. p. 46·5°) had been introduced into it. On cooling to about 15°, crystallisation occurred, and nearly the whole of the liquid became solid. The crystals thus obtained melted at 17°, that is, 28° lower than the original substance. Many similar observations have been made, and it has been invariably found that on heating the aldoxime the freezing point of the liquid is lowered to a greater or less extent. On heating the crystals (m. p. 46·5°) for two hours at 100° in a closed tube, no apparent chemical change occurred and the liquid still boiled constantly at 114·5°, but on cooling to 0°, it solidified to a mass of crystals melting at 12° (corr.) to a liquid which froze again within half a degree of the same temperature. No further lowering of the freezing point was caused by heating this substance for two hours in a closed tube at 150°; the resulting liquid again crystallised at 12°.

We had thus obtained evidence that a change in the constitution of acetaldoxime occurs when it is heated, the original substance (m. p. 46·5°) being gradually converted into a new modification which melts at 12°. This observation explains why the liquid purified by distillation refuses to crystallise at the ordinary temperature, and may account for the circumstance that the crystallisation of acetaldoxime has not been previously observed.

The properties of the modification melting at 12° are still under investigation. We find that on standing at the ordinary temperature it slowly changes back again into the substance which melts at 46·5°; the melting point of the crystals gradually rises from day to day until the maximum of 46·5° is reached. Conversely, when the original crystals (m. p. 46·5°) are melted and the liquid gently heated, the freezing-point of a specimen removed from time to time is observed to fall gradually as the heating is continued until it reaches the minimum at 12°; even in determining the melting point this change occurs to some extent, and if the freezing point of the resulting liquid is at once determined, it will usually be found to be several degrees lower than the melting point, owing to the conversion having occurred with formation of a small quantity of the new modification, which depresses the freezing point of the liquid. For the same reason, freshly distilled aldoxime always contains some of the new modification and therefore freezes at a lower temperature than 46·5°.

So far we have not observed any fact connected with this behaviour of acetaldoxime which bears any other intepretation than that we have already indicated. It appears that, contrary to the usual statement, acetaldoxime is a crystalline solid, capable of existing in two isomeric or polymeric forms, which readily change the one into the other. The form melting at 46·5°, which is solid at ordinary temperatures, may be provisionally designated *α-acetaldoxime*, whilst that melting at 12°, which is liquid at ordinary temperatures, may be termed *β-acetaldoxime*.

During the last six months we have been engaged in examining the physical and chemical properties of the two substances, with a view of discovering other differences between them. Dr. Perkin has kindly undertaken to study the variations in magnetic rotation which may accompany the conversion of the one form into the other. It was not our intention to give any account of our results until all these experiments, now in progress, were completed; we are, however, compelled to publish the main facts at once, on account of the appearance of a preliminary note by the Dutch chemist Franchimont, of which we have just been made aware through the *Chemische Centralblatt*. This chemist has observed the solidification of a specimen of acetaldoxime which had been purchased by him from Kahlbaum and he states that he is now searching for evidence of an isomeride. We trust that the publication of some of our observations will serve to convince him of our priority in this matter, and that he will leave us free to finish the experiments which have been in progress during the past ten months.

The existence of two isomeric acetaldoximes has important theoretical bearings which we have steadily kept in view during the course of our work. Hantzsch, as well as other chemists, have sought for evidence of isomerism, but have failed to find any but the one acetaldoxime hitherto regarded as liquid. We shall shortly be able to state whether this is a case of isomerism or polymerism, and if the former, whether it must be considered as stereochemical or structural. In the latter case we have the two possible structural formulæ $CH_3{\cdot}CH{:}NOH$ and  $CH_3{\cdot}CH<\overset{NH}{\underset{O}{|}}$. In fact, we should have to deal with the same problem as that presented by the two far more stable benzaldoximes which has been investigated, among others, by Hantzsch, Victor Meyer, and Beckmann, and the difficulties standing in the way, both of experiment and of correct interpretation, are certainly not less than they were in that now classical enquiry.

In conclusion, we may mention that we have lately found a simple means of preparing acetaldoxime, which is both more convenient and economical that that originally proposed by Victor Meyer and now generally adopted. We find that an almost theoretical yield of the compound results from the interaction of aldehyde-ammonia and hydroxylamine hydrochloride, thus:—$CH_3{\cdot}CHO,NH_3 + NH_2{\cdot}OH,HCl = NH_4Cl + H_2O + CH_3{\cdot}CH{:}N{\cdot}OH$. When the proper quantities of these materials are mixed together, the mixture becomes semi-liquid. The acetaldoxime is dissolved out with ether, the ethereal solution dried with calcium chloride, and the ether carefully removed by distillation at as low a temperature as possible. The residual acetaldoxime is then distilled. The distillate, boiling at 114·5°, being a mixture of the α- and β-modifications, will probably not crystallise unless it is cooled, when it will almost entirely solidify to a mass of crystals, which usually form a network of long, stout, flexible needles, remarkable for their toughness. On keeping, it will be found that the melting point of these crystals gradually rises to 46·5°.

Research Laboratory, Pharmaceutical Society,
Bloomsbury Square, London.

ANNUAL GENERAL MEETING,

March 30th, 1892.

Professor A. Crum Brown, F.R.S., President, in the Chair.

I AM glad to say that our Society continues prosperous, and that our numbers increase. At the present time there are 1825 Fellows of the Society and 30 Foreign Members, 1855 in all.

The Society has to deplore the loss of two veteran Foreign Members, Hermann Kopp and Jean Servais Stas. The Treasurer has undertaken to give an account of the work of the former and to sketch the modern development of his ideas in a lecture to be delivered during the coming session. It is hoped that in like manner justice may be done to the work of Stas by one of the Fellows specially qualified to deal with such a subject.

The following tabular statement gives the numerical position of the Society:—

Number of Fellows (Anniversary, March, 1891)		1754
Since elected and paid admission fees		120
		1874
Removed on account of arrears	18	
Withdrawn	18	
Deceased	13	
		49
Present number of Fellows		1825
Number of Foreign Members (1891)	32	
Deceased	2	
Present number of Foreign Members		30

The number of Fellows elected this year is somewhat greater than last year, but still falls considerably below what it was in 1889–90.

13 Fellows have died within the year:—Dr. J. H. Abrahall, Dr. A. J. Bernays, Chas. Heisch, H. J. Hardy, T. H. Hills, J. S. Jackson, J. B. Mackintosh, C. McNally, J. W. Pratt, Dr. Redwood, A. J. Shilton, Dr. Tidy and P. H. Wright.

18 Fellows have withdrawn:—H. H. Bunting, W. L. Clarke, W. Y. Dent, Rev. G. R. Faulkner, Robt. Ferguson, Thos. Hilditch, Rev.

T. Lindsay, Wm. Robinson, J. B. Readman, W. H. Reid, Chas. T. Sprague, George Sutcliffe, C. H. Sieber, Saml. D. Wills, J. C. Watson, W. C. Wise, Prof. E. Marks and D. T. C. Charles, whilst 18 Fellows have been removed on account of arrears.

The Library slowly and steadily increases, and now contains 12,209 volumes. The precise increase will be seen from the subjoined tabular statement:—

	March 30th, 1891.	Additions in 1891–92.	Present State.
Volumes of systematic works..........	3,204	110	3,314
Volumes of periodicals...............	5,870	245	6,115
Volumes of duplicate periodicals for circulation	1,188	78	1,266
Pamphlets........................	1,472	42	1,514
	11,734	475	12,209

No fewer than 128 papers have been read, the largest number on record. The 1891 volume of the Transactions contains 95 original papers, occupying 1100 pages, while the Abstracts occupy 1564 pages.

At the commencement of the winter session Professor Attfield brought under the notice of the Council his proposal for establishing a Chemists' Benevolent Fund. A Committee was appointed to consider this proposal, and eventually they presented a Report, which will be found in full in the Proceedings, pp. 60—64.

A Committee of the Council have had under consideration the question of the entire rearrangement, ventilation, and lighting of the meeting room, and with the cooperation of Professor Ayrton and Mr. Martin L. Saunders (architect) have prepared a scheme which is now under the consideration of Her Majesty's Office of Works; if approved, this will be carried into effect during the long vacation.

We may divide chemical work roughly into two kinds: routine work —analysing, teaching, examining, and so on—and what is often, though not very appropriately called, "research"—I shall, on this occasion, call it exploration. In the first kind we chiefly use methods and deal with facts already known; in the second we devise new methods and make the acquaintance of facts before unobserved, or, at least, unrecorded. The first kind is, as a rule, undertaken as a matter of business; the second, as a rule, as a matter of pleasure. The distinction between them is not sharp—routine work not unfrequently leads to fresh fields of knowledge—much of our store of analytical methods has been obtained in the course of specific analyses not undertaken for the purpose of devising new methods—and, indeed, in chemistry, as in the world generally, an intelligent person cannot walk anywhere with his eyes open without seeing something new; on the other hand, exploration may degenerate so as to become as uninteresting and as mechanical as the barest kind of routine work; yet every one will recognise that the division is a natural one, and, in most cases, we can have no difficulty in saying upon which kind of work we are at any time engaged. Each of these kinds of work is, I believe, best done by a man who does not confine himself to it. The man whose daily business is, say, to teach or to assay, will teach or assay better if he takes what we may call an occasional exploratory tour, just as a weaver or a printer is not only a healthier man, but better at his work, for a turn now and then in the fresh air. And, I believe, it is equally true, that a man whose main work is exploratory—a man placed by fortune in such a position that he can devote his whole time to it—will be better, and do better work, if he undertakes some routine duty. There is a satisfaction in having accomplished a task, different in kind and different in moral effect from the joy we feel when we have reached some untrodden peak, and look out from it over a new region. I have fallen into a geographical metaphor, and may as well continue in it while speaking of exploratory work, and consider it as either internal or frontier work. So much of the interior of every district in the country of chemistry is unexplored, or only very imperfectly known, that our surveyors are mostly taken up with internal exploration and mapping, but the frontiers have a special interest of their own. It is through them that we may hope to join our survey—the great, general triangulations of the chemical country—with the surveys, some more complete, some less complete, than ours, which our neighbours have made and are making. One very important branch of this frontier work—purely chemical work bearing directly on neighbouring sciences—is the artificial production of natural substances. The artificial production of minerals is chemical work, but it is of more immediate and practical interest to mineralogists and physical geologists than to chemists. Work of this kind has often to wait until a man appears who unites the two requirements—interest in the work and ability to do it.

The artificial production of substances occurring in plants and animals is more attractive to chemists, and a large part of our knowledge of organic chemistry has been obtained by means of attempts, some successful and some not, in this direction. All work of this sort is interesting to chemists, as all organic synthesis is, and at first sight we might expect that it would have a special interest for physiologists. But this is only rarely the case, and on looking at the matter we easily see why. Most of our organic syntheses of natural substances are made by methods and under conditions quite unlike anything that occurs in nature. In nature's organic laboratory there is no pentachloride of phosphorus, no strong nitric or sulphuric acid, no free halogens, no alcoholic caustic potash; there are no sealed tube operations, no distillation *in vacuo;* the temperature is never higher than about 40° C., and every operation is carried on in the presence of much water. How few of our syntheses could be performed under such conditions! It thus happens that the great majority of organic syntheses are uninteresting to the physiologist, because they do not follow the lines of the synthesis which occurs in nature.

Organic synthesis, as we effect it, with those powerful appliances which we use, and nature does not, will no doubt ultimately be of service to physiology. Much of the evidence for the constitution of a substance is obtained from a study of the ways in which we can make it, and when we know its constitution we can often spy out new modes of synthesis, and among these we may find some which can be carried out under nature's conditions; but as yet we know few such.

There are exceptions, and among these I may refer to the brilliant work of Professor Fischer on the synthesis of glucose, fructose, &c. This great investigation, which every chemist has followed with interest and pleasure, throws real and direct light on the processes by which the plant builds up carbohydrates from formic aldehyde. This is really frontier work, and by such lines we may hope to gain insight into the methods of nature's organic laboratory, as mineral synthesis is enabling us to understand how the dead framework of the earth arrived at its present state.

Another frontier of chemistry is that which looks towards those regions of physics which have come more or less completely under the control of the great empire of mathematics. And here both the work done from our side and that done from the mathematico-physical side has special interest for us. For we may expect chemistry to undergo a very great and revolutionary change when that frontier comes to be explored and cultivated. We shall then be separated by an imaginary line from the mathematical sciences, and mathematical methods will rapidly be applied to chemical questions. Chemical methods will still be used. The most perfect dynamical explanation of chemical constitution and chemical change will not enable us to dispense with the old processes of analysis and preparation. The chemist will still be the man trained in the chemical laboratory, and all the mechanical parts of the work will still be done by him. But, unless he learns the language of the empire, he will become a provincial, and the higher branches of chemical work, those which require reason as well as skill, will gradually pass out of his hands. This must not be, and the younger chemists can prevent it. Let them while there is time learn the language of the empire. Let them become fluent and ready in its use; let them read with care the work that is being done on the border between chemistry and mathematical physics, and, as they find opportunity, do such work themselves, and so be ready to take their part in the union which will certainly come.

The language of the empire is not the kind of mathematics that boys are usually taught at school; it is not the kind of mathematics that medical and science candidates have to pass at a preliminary or first B.Sc. examination; it is mathematics *for use*. It bears to what we may call examination mathematics the same sort of relation that French and German *for use* bear to much of our school French and German, and the way to learn it is to work with it.

I feel some delicacy in referring to particular cases of work on the frontier between chemistry and mathematical physics, because I do not think it my duty here to enter into criticism of disputable matter. It has not been the custom for the Fellows of the Society at the Annual Meeting to criticise the President's address, and it is better that the address should rather be suggestive than polemic. It is therefore not in a critical spirit that I speak of the theories propounded by Van't Hoff and by Arrhenius. Whether these theories are ultimately accepted or rejected by chemists and by physicists, we must all admit that they have been productive of important work, and that they have set us all thinking about matters which it is necessary we should look at from all sides.

Before we can profitably criticise a theory, we must understand it, and most of us have, I believe, found some difficulty in understanding the theories of osmotic pressure and the dissociation of ions. I do not blame the preachers of the new doctrines for this, although they might have been more explanatory, nor do I think those of us who have felt these difficulties have any reason to confess exceptional dulness. The doctrines *are* novel and strange, and no mode of presenting them could have made them easy. It is, of course, possible to understand them; the question is, is it worth while? Believing it to be worth while, I took some trouble in the matter, and may perhaps be of use to those, if there are any, who are now struggling with the difficulties which perplexed and, to some extent, still perplex me. I hope those of you who have never felt these difficulties will pardon my taking up their time with two of them.

The first has reference to the very idea of osmotic pressure. We have a membrane with water on one side, and a solution on the other; although the hydrostatic pressure is the same on the two sides, water goes through from the water side to the solution side. We should naturally suppose that this implies the existence of a pressure which drives the water through, and can be measured by the hydrostatic pressure which has to be applied from the solution side, so as to balance it and prevent water going through. But the "osmotic pressure" of the theory is from the solution against the membrane, contrary to the direction in which the water flows. To reconcile this paradox, we must consider the nature of the osmotic pressure of the theory. The thinnest, most delicate septum interposed between the solution and the water is unaffected by the osmotic pressure, if it is impermeable to water. Indeed, a membrane permeable to the solvent and impermeable to the thing dissolved, is necessary, not only for making observations on "osmotic pressure," but even for forming a conception of it, and therefore, whenever we come to a difficulty, we shall only get into more confusion if we try to reason out the case by means of ideas connected with ordinary pressure. We must go back to the real, practical definition of osmotic pressure as the difference between the hydrostatic pressure on the two sides of the membrane permeable to the solvent, impermeable to the thing dissolved, when there is equilibrium.

An analogy which has been used to make the thing clearer does not get over the real difficulty. We are asked to suppose a cell completely surrounded by a thin wall of palladium, and containing nitrogen at pressure p_1. The cell is placed in a vessel containing hydrogen, kept always at pressure p_2. It is assumed that, as palladium is permeable to hydrogen and not to nitrogen, hydrogen will go in until the partial pressure of the hydrogen in the cell is equal to the pressure outside, that is, to p_2. The pressure inside will, when equilibrium is established, be $p_1 + p_2$. Here it is said p_1, the difference of pressure on the two sides of the semipermeable palladium, corresponds to the osmotic pressure. The analogy holds to a certain extent, and I have experienced its helpfulness, but there is this essential difference, that the pressure of the enclosed nitrogen can be quite well measured by means, say, of an impermeable piston, before the cell is put into the vessel of hydrogen at all. The final pressure in the palladium cell is the original inside pressure *plus* the outside pressure; whereas the semipermeable membrane with solvent outside is necessary for the mere observation of osmotic pressure, and the final pressure in the osmotic cell may be much greater than the sum of the external pressure and the original internal pressure.*

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* If we assume that, as it is the excess of hydrogen pressure outside over the hydrogen pressure inside that drives the hydrogen in through the palladium, so it is

The second difficulty I have to speak of is connected with the doctrine of the dissociation of the ions.

Let us imagine a mixture of hydrogen and chlorine in the proportion in which they unite placed in a closed vessel kept in the dark, at ordinary pressure, and at such a temperature that no combination occurs. Here we have the hydrogen and the chlorine particles (molecules) moving freely about among each other, each at its own proper speed, colliding and rebounding, but, under the pressure and at the temperature we are supposing, practically uninfluenced otherwise by each other's presence. (If an opportunity were given for diffusion into an indifferent gas, the hydrogen would to a large extent diffuse away, leaving in the vessel a mixture containing a large excess of chlorine.) Let us now suppose a spark passed through the vessel; combination occurs; much heat is given out. We find that the hydrogen and chlorine no longer move independently; diffusion does not separate them. Dissolve the hydrochloric acid gas in water, and so make a dilute solution. More heat is given out, and yet the theory asserts that in this dilute solution the hydrogen and chlorine particles are moving about among each other as independently as in the gas, nay, that there is in the dilute solution an additional kind of freedom, as the particles are single atoms and not pairs, as in the mixture of hydrogen and chlorine gas.

And, according to the theory, these hydrogen atoms are moving at a speed proper to them, and the chlorine atoms at a speed—much less—proper to them, but they do not now diffuse away from one another, if the solution is placed in contact with pure water. What diffuses is hydrochloric acid, or, according to the theory, hydrogen and chlorine atoms in equal numbers. We have, then, decomposition of hydrochloric acid without absorption of heat and independent movement of hydrogen and chlorine atoms at different speeds without the possibility of separation by diffusion. This apparent paradox has stumbled many. The solution of the paradox turns, as you all know, on the electric charges of the ions; but instead of saying again, what has been better said by Ostwald and other advocates of the theory, I shall conclude with a sort of parable, leaving its application to you.

A parable is not a strict analogy—it does not fit at every point—but it may help the imagination where it needs help, and only a very simple person will be misled by such parts of the parable as do not fit.

the excess of water pressure outside over water pressure inside that drives the water in through the semipermeable wall of the osmotic cell, we come to the conclusion that, in a solution at ordinary pressure, the partial pressure of the *water* is often negative. This is not an absurdity, and there is no insurmountable difficulty in reconciling it with the theory of the cause of osmotic pressure.

Let us suppose a nomad tribe, consisting of 1,000 or 1,000,000, or any large number you please, of men, all exactly alike, and each the owner of a cow. The cows, which are all exactly alike, are all private property, but the land is common, and each man, accompanied always by his cow, moves about from place to place within the territory of the tribe. The men meet one another every now and then, but only exchange a word or two, and move off, each with his cow. Now we shall suppose a change of climate, or an accession of territory, or other change of circumstances, such that it is found more convenient that, instead of each man owning a single cow—his very own—a number of men club together, so that each man of the n members of the club has one share in the property of the club, that is $1/n$th share of n cows. He gets a share certificate, and the cows are marked as club property. A member of the club need no longer accompany his cow everywhere—he has no particular cow—he can go about independently *wherever there are club cows*, attending to such as he comes across. But his interest in the club property (his property) prevents his wandering away where there are no club cows, and, similarly, club cows may go about freely *wherever there are club members*, but are not allowed to wander away to places where there are none. No one looking at this new state of society would say, "These men have given up their cows for nothing." They have not given them up. They still possess them, and if you want them you will have to pay for them, just as you would have had to pay the individual owners.

Co-existent with such a club there might be private ownership; indeed, the proportion of club members to private owners would depend on the extent to which the change favourable to club life had gone. We may further suppose that the men are not all alike, and that some joined the club with two cows each, some with horses—each member's share certificates corresponding to the property he brought in. If circumstances change, so that club life becomes rather less advantageous, some members will be paid off, giving up their share certificates and getting each a cow or a horse or two cows (from which, of course, the club mark is removed), according to the number of his share certificates, the club always retaining those members and that kind of property most suitable for the club.

I might pursue the matter further, and speak of a tinman who, having originally two shares, steals a share from each of two ironmen, who have three each, and goes about with four shares, and is sometimes paid off at that rate, while his victims have to do with two each; but I forbear.

I have presented these remarks, not as arguments in favour of the new theories—they are useless for that purpose—but as helps towards understanding them.

We are sometimes asked if we believe such and such a theory to be true. The question is really an absurd one. It ought to be, Is the theory applicable, is it likely to be productive, does it lead to clearer notions as to the relation of phenomena to one another, and so towards wider, more generally applicable, more useful theories? Answers to these questions will soon accumulate—answers either affirmative or negative, which will make the discussion of the truth of a theory a needless one.

Sir Henry Roscoe proposed a vote of thanks to the President, coupled with the request that he allow his address to be printed. Dr. Gladstone seconded the motion, which was carried by acclamation. The President having thanked the meeting,.

Professor Thorpe, the Treasurer, gave an account of the balance sheet which he laid before the Society duly audited. The receipts had been:—By admission fees and subscriptions, £3545; by sale of Journal, £408 7*s.* 4*d.*; and by dividends on invested capital, £367 12*s.* 10*d.* The expenses had been:—On account of the Journal, £2798 15*s.* 10*d.*; on account of the Proceedings, £159 14*s.* 5*d.*; on account of the Library, £277 6*s.* 2*d.*; the total expenditure being £3989 1*s.* 6*d.* Grants amounting to £406 5*s.* 4*d.* had been made to Fellows from the Research Fund during the year. As illustrating the growth of the Society's work, the Treasurer mentioned that whereas the expenditure on the Journal had been only £1733 11*s.* 10*d.* in 1882, in 1887 it had risen to £2026 16*s.* 9*d.*, and this year amounted to £2798 15*s.* 10*d.* He anticipated that the proposed alterations and redecorations of the Society's rooms during the coming long vacation would absorb nearly £1000 of the balance now at the bank.

Mr. David Howard proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Professor E. Frankland.

Sir Henry Roscoe having asked for information with reference to the Report of the Jubilee Meeting, and with regard to the Learned Societies' Registration Bill, both items of charge in the balance sheet, Dr. Armstrong said that the former was in hand, and would ere long be ready for issue; unfortunately they had been unable to induce any Government Department to take charge of the Registration Bill, and he feared that there was but little chance of getting it brought forward unless promoted as a private measure.

Mr. Cassall, after a reference to the cost of printing the suggested alterations in the bye-laws, which he supposed was included in the cost of printing the Proceedings, asked the President whether he had received a letter, and was prepared to consider the request therein made that he would inspect the documents in which a number of

Fellows of the Society had expressed their wishes with reference to the suggested alterations in the bye-laws.

The President replied that he had received a letter signed by Dr. Teed and Mr. Cassall, and that he could only say that a letter from even one Fellow of the Society would meet with every consideration from him.

The vote of thanks to the Treasurer having been passed, the Treasurer proposed a vote of thanks to the Auditors, mentioning that he was much indebted to Mr. Tutton for his assistance in connection with the accounts. Professor Ramsay seconded the motion, which was unanimously adopted, and acknowledged by Mr. Dyer.

Professor Odling then proposed a vote of thanks to the Council and Officers, including the Editors, Abstractors, and Librarian. Mr. Carteighe supported the motion, which was adopted. Dr. Armstrong and Mr. Groves having replied,

Scrutators were appointed, and a ballot was then taken for the election of Officers and Council for the ensuing year: the following were subsequently declared elected.

President: Dr. A. Crum Brown, F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, K.C.B., D.C.L., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: A. Vernon Harcourt, F.R.S.; W. N. Hartley, F.R.S.; John Pattinson; William Ramsay, F.R.S.; William A. Tilden, F.R.S.; Robert Warington, F.R.S.

Secretaries: H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary: Raphael Meldola, F.R.S.

Treasurer: T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council: Henry Bassett; Norman Collie, Ph.D.; Harold Dixon, F.R.S.; John Ferguson, M.A.; R. J. Friswell; John Heron; M. M. P. Muir; F. J. M. Page; W. H. Perkin, jun., F.R.S.; S. U. Pickering, M.A.; John A. Voelcker, Ph.D.; W. P. Wynne, B.Sc.

DR. THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY FROM MARCH 19TH, 1891, TILL MARCH 18TH, 1892. CR.

	£	s.	d.	£	s.	d.
Balance at Bank March 19th, 1891	1,798	17	7			
,, in hands of Treasurer	2	8	7	1,801	6	2
Receipts by Life Compositions, Admission Fees, and Subscriptions from March 19th, 1891, to March 18th, 1892.						
20 Life Compositions at £20	400	0	0			
119 Admission Fees at £4	476	0	0			
1 Subscription for 1887 at £2	2	0	0			
2 Subscriptions for 1888 at £2	4	0	0			
19 ,, ,, 1889 at £2	38	0	0			
93 ,, ,, 1890 at £2	186	0	0			
361 ,, ,, 1891 at £2	722	0	0			
4 ,, ,, ,, at £1	4	0	0			
841 ,, ,, 1892 at £2	1,682	0	0			
27 ,, ,, ,, at £1	27	0	0			
2 ,, ,, 1893 at £2	4	0	0	3,545	0	0
Sale of Journal				408	7	4
Subscriptions for Royal Society Proceedings				5	0	0
Subscription from Institute of Chemistry				10	15	0
,, from Society of Chemical Industry				6	6	0
,, ,, ,, Public Analysts				4	4	0
Year's Dividends on £6,730 Metropolitan Board of Works 3½ per cent. Stock				229	13	4
Year's Dividends on £4,000 Consols				107	5	0
Year's Dividends on £788 London and North Western Railway Debenture Stock				30	14	6
Assets.						
Balance at Bank	2,158	12	3			
,, in hands of Treasurer	0	17	7			
3 per cent. Consols	4,000	0	0			
Metropolitan Board of Works 3½ per cent. Stock	6,730	0	0			
London and North Western Railway Debenture Stock	788	0	0			
	13,677	9	10	6,148	11	4

	£	s.	d.	£	s.	d.
Expenses on Account of the Journal.						
Salary of the Editor	300	0	0			
Salary of the Sub-Editor	150	0	0			
Editor's Postages	4	13	1			
Fees to Abstractors	356	9	7			
Periodicals for Abstractors	10	4	0			
Printing of Journal	1,625	18	8			
Distribution of Journal	351	10	6	2,798	15	10
Expenses on Account of the Library.						
Salary of Librarian	50	0	0			
,, Library Attendant	62	0	0			
Books and Periodicals	121	1	11			
Binding	32	7	3			
New Bookcases	11	17	0	277	6	2
Printing Authors' Copies				62	14	6
Printing and Distribution of Abstracts of Proceedings				159	14	5
Miscellaneous Printing				60	9	3
Stationery				30	15	1
Inhabited House Duty and Income-tax				7	8	9
Repairs				17	18	10
Testimonials to Prof. Stas and to the Pharmaceutical society				9	9	0
Longstaff Medal				1	10	0
Expenses in connection with Jubilee Celebration				59	0	2
,, ,, ,, Captain Abney's Lecture				13	13	0
Parliamentary and Legal Expenses				64	18	10
Photographic Enlargements for Council Room				11	11	0
Actuarial Fee				5	5	0
Insurance				30	0	0
House Expenses.						
Providing Refreshments	18	19	4			
Lighting the Building (gas)	58	3	1			
Heating ,, (coals)	19	13	6			
Cleaning ,,	12	18	4			
Petty House Expenses	7	17	6			
House Porter's Wages	65	0	0			
Gate Porter and Watchman	2	2	0	184	13	9
Collector's Commission on Subscriptions (5 per cent. on £3,545)				177	5	0
Treasurer's Stamps and Drafts				5	15	11
Honorarium to Treasurer's Assistant				10	0	0
Treasurer's Petty Cash Disbursements				0	17	0
Balance at Bank {on Deposit, £1,000; General Account, £1,158 12s. 3d.}				2,158	12	3
,, in hands of Treasurer				0	17	7
				6,148	11	4

Audited, with vouchers, and found correct.
March 19th, 1892.

HOLLAND CROMPTON.
BERNARD DYER.
THOMAS S. DYMOND.

TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH RESEARCH FUND.
FROM MARCH 19TH, 1891, TILL MARCH 18TH, 1892.

DR.

Date	Item	£	s.	d.
1891. Mar. 19.	Balance at Bank	217	2	4
	Year's Dividends on £1,000 North British Railway 4 per cent. Stock	39	0	0
	Year's Dividends on £4,400 Metropolitan Board of Works 3½ per cent. Stock	150	3	0
		£406	5	4

Assets.

	£	s.	d.
Metropolitan Board of Works 3½ per cent. Stock	4,400	0	0
North British Railway 4 per cent. Stock	1,000	0	0
Balance at Bank	66	5	4
	£5,466	5	4

CR.

Date	Item	£	s.	d.
April, 1891.	Honorarium to Dr. Japp, with Longstaff Medal	20	0	0
May, 1891.	Grant to Prof. W. H. Perkin, jun.	75	0	0
,,	,, Mr. A. E. Tutton	10	0	0
,,	,, Mr. J. J. Sudborough	10	0	0
,,	,, Dr. E. H. Cook	5	0	0
July, 1891.	,, Mr. W. Sinclair	15	0	0
,,	,, Mr. J. Stenhouse	10	0	0
,,	,, Mr. G. Young	10	0	0
,,	,, Dr. J. M. H. Munro	25	0	0
,,	,, Mr. G. H. Robertson	10	0	0
,,	,, Mr. A. R. Ling	10	0	0
,,	,, Dr. S. Ruhemann	10	0	0
Jan., 1892.	,, Dr. W. F. Laycock	5	0	0
,,	,, Mr. J. Leicester	10	0	0
,,	,, Messrs. Linder and Picton	10	0	0
,,	,, Messrs. Cross and Bevan	25	0	0
,,	,, Prof. A. Smithells	50	0	0
,,	,, Dr. J. Walker	15	0	0
,,	,, Mr. W. P. Wynne	15	0	0
	Balance at Bank	66	5	4
		£406	5	4

Audited, with vouchers, and
found correct,
March 19th, 1892.

HOLLAND CROMPTON.
BERNARD DYER.
THOMAS S. DYMOND.

OBITUARY NOTICES.

By the untimely death of JOHN LEIGH HOSKYNS-ABRAHALL, at the age of 26, English science loses one who would have added to its laurels. Leigh Abrahall was born in 1865 at Combe (near Woodstock), of which place his father, the Rev. John Hoskyns-Abrahall, M.A. (a distinguished scholar), was vicar. He received his early education at the Forest School, Walthamstow, under Dr. Guy, and at Eton College, where he held a King's Scholarship. From Eton he went, in 1884, with a demyship, to Magdalen College, Oxford. At this university he took a second class in Mathematical Moderations and a first class in the Final Honours School of Chemistry. During his stay at Oxford, and while working under the direction of Professor Odling, he published an original research on phenylsulphonic anhydride, a compound which he succeeded in preparing in the pure state for the first time. He proceeded to the degree of B.A. in 1887, and his demyship was then renewed to him by his college, to enable him to study at Munich in Professor Baeyer's laboratory. Here he worked with Dr. Bamberger on the "alicyclic" 1 : 5-tetrahydrodiamidonaphthalene, a compound of considerable importance in connection with Bamberger's remarkable researches on the hydronaphthylamines; he was, however, much to his regret, forced to abandon the subject, owing to repeated attacks of eczema, brought on by the compounds under investigation. He then migrated to Professor Groth's mineralogical laboratory, where he worked at crystallography, and carried out a series of careful analyses of pure apatites of various origins. These analyses led him to a conclusion which differs from those put forward by previous observers. He assigns to apatite the formula $Ca_{10}(PO_4)_6(F_2,Cl_2,O)$, the fluorine and chlorine being replaceable in isomorphous crystals by equivalent amounts of oxygen, as Marignac, in 1865, had found to be the case in the fluoroxyniobates, fluoroxytantalates, fluoroxytungstates, &c. This work was published as an inaugural dissertation, and obtained for the author the doctor's degree at the University of Munich.* In December, 1888, Abrahall was elected a Bishop Berkeley Fellow of the Owens College, Manchester, and on the expiration of this fellowship he was elected to an honorary research fellowship, which he held until his death. Nearly the whole of his working time in Professor Dixon's laboratory was given to a research on the atomic weight of boron, the details of which will shortly be published. His results show that the atomic weight of boron must be reduced from 11, the number given by Berzelius, to about 10·8. The determination was a difficult and delicate one, and Abrahall spared no pains in making it as accurate as possible. The final results, agreeing as they do to within 1/5000 of their value, would, however, scarcely have satisfied the author had he lived to calculate them out himself, and he would, doubtless, have continued and completed the work, for which he left a certain amount of pure material.

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* An original essay on isomorphism, in which the views of previous observers are criticised in detail, was doubtless suggested by this investigation; it was unfortunately left in a fragmentary state.

Abrahall had the qualities which make a true chemist—scientific culture and imagination, manual dexterity, and the most unyielding patience and determination in overcoming difficulties. It was not unusual for him to spend 10 or 12 hours continuously in the laboratory. He found relaxation in the study of languages (Icelandic, Russian, and Greek), in sketching, and in taking long walks. As a walker and climber he was indefatigable. During vacations spent in the Tyrol and in Iceland, he spent days on the mountains alone and without a guide. On his return from Iceland he published an interesting account of a visit to the unique quarry of Iceland spar at Eskifjördhr. In August of last year he set out with his father for a journey to Italy, Sicily, and Greece, of which he has left a record in a series of letters full of vivid description and delightful touches of humour. They tell, too, of the indomitable physical energy of the writer, and of a personal recklessness which, unfortunately proved fatal. Abrahall seems not to have realised the danger of passing the night in the open in the treacherous southern climates; he slept on the bare ground on the sides of Vesuvius and Etna, and on the marshy plains of Greece. Here both he and his father contracted malarial ague, to which they succumbed within a week of one another, shortly after their return home. Leigh Abrahall died at Bedford, on October 12th, 1891. Unconventional and outspoken to a fault, though full of gentleness and courtesy, he cared nothing for personal advancement, and mixed little with the world. His near friends will long miss his presence. They will keep the memory of a life of which work and achievement were the sole ideals.

The titles of J. L. Hoskyns-Abrahall's papers are as follows:—"On Phenylsulphonic Anhydride" (*Journ. Chem. Soc.*, 1886, 692), "Ueber 1 : 5-ac.-Tetrahydronaphtylendiamin" (*Ber.*, 1889, 943), "Ueber die Zusammensetzung des Apatits" (*Inaugural Dissertation*, Munich, H. Kutzner, 1889), "A Visit to the Calcite Quarry in Iceland" (*Mineralogical Magazine*, **9**, 179), "On the Atomic Weight of Boron" (Preliminary abstract, *Proc. Chem. Soc.*, 1892), "An Ascent of Etna" (a letter published posthumously in the *Manchester Guardian*, April 19th, 1892"), "On the Atomic Weight of Boron" (a posthumous paper), "On (Chemical) Stability" (an unpublished mathematical paper, in which original views are put forward, read before the Owens College Chemical Society in 1889). P. T. H.

Albert James Bernays was born in London in 1823, and was the son of a well-known professor of languages at King's College. He was educated at King's College School, and subsequently studied chemistry under Fresenius and Liebig, taking the degree of Ph.D. at Giessen.

In 1845 Dr. Bernays established a laboratory in Derby, lectured on Agricultural Chemistry, and soon became known in that town from the interest he took in questions relating to food and hygiene. He also lectured in Newcastle-on-Tyne. Whilst resident in Derby he published a book on *Household Chemistry*, which ran through several editions. In 1851 he served as a juror at the Great Exhibition, and it was in this year that he discovered *limonin*, the bitter principle of the pips of lemons, oranges, &c.

In 1855 Dr. Bernays was appointed Lecturer on Chemistry in the Medical School of St. Mary's Hospital, a post which he resigned in 1860, on his appointment to a similar lecturership at St. Thomas's Hospital. Here he lectured on chemistry and on toxicology till his death. His care and exactitude, coupled with a lucid manner of exposition, made him a sound and effective teacher, and as such he was fully appreciated by his colleagues and pupils. His warmth of heart, honesty of character, and deep interest in the welfare of medical students are held in grateful recollection by successive generations of his pupils.

In the Metropolis, Dr. Bernays soon became a recognised authority on many questions of hygiene and applied chemistry, and his contributions to applied chemistry were numerous. Among these may be mentioned his "Investigations on the Atmosphere of Cornish Mines," and "Dangerous Trades," and his inventions in water filtration; also his researches on the analysis of water and food. He also published several manuals for the use of students and others, and held many important posts of public analyst, and was for many years consulting chemist and analyst to the Kent Water Company.

In addition to his scientific labours, Dr. Bernays took a deep and active interest in social matters, and was an effective public speaker. To the last, the welfare of those around him actively engaged his attention; and in proof of this it may be mentioned that he delivered over a thousand free lectures on such subjects as food, health, explosions in mines, cremation, &c. He died at Brixton on January 5, 1892, in his 69th year, after a brief illness; and by his desire his remains were cremated. T. S.

THOMAS HYDE HILLS was born at Maidstone in 1815, and was educated first at the local Grammar School, and subsequently at Gondhurst, Kent. In 1830, he was apprenticed to Mr. Thorby, chemist, of Brighton, but left there in 1837, and came to London, where he entered the well-known pharmaceutical establishment of John Bell and Co., Oxford Street. In 1848 he became a partner in the firm, and in 1859, on the death of Jacob Bell, sole proprietor.

Mr. Hills was intimately associated with the rise and progress of the Pharmaceutical Society, established in 1841 mainly owing to the efforts of his friend and partner Jacob Bell. He was elected to the Council in 1860, was Vice-President from 1863 to 1868, Treasurer from 1868 to 1873, and President from 1873 to 1876. He retired from the Council of the Pharmaceutical Society in 1881.

Mr. Hills was elected a Member of the Council of the Chemical Society in 1877. He died on November 19, 1891, after a lingering and protracted illness.

Mr. Hills was well known in the scientific and artistic circles of London. Although he was not an original worker in science, he took a deep interest in its advancement, and was continually stimulating and encouraging others to devote their energies to original research. In connection with the Chemical Society, an effort was made by him in 1872 to institute and maintain a small special fund to be expended in money grants to investigators, and for this purpose he presented the Society with a donation of £10, and offered the continuance of a like donation for several years under conditions intended to elicit co-operation. Although this proposal did not at the time meet with the response which it merited, the suggestion was, a few years later, owing to the liberality of Dr. Longstaff and others, realised in the establishment of the Chemical Research Fund. It may also be added that the appointment for the first time of a Professor of Chemistry in the Royal Academy of Arts in London was largely due to Mr. Hill's persevering efforts among his Academician friends.

The death of Thomas Hyde Hills removes one who by his generous and kindly encouragement did much to aid the progress of chemical science, and there are many successful Fellows of the Society who have reason to feel specially grateful to him for assistance and kindly counsel in their young days. By these and many others who knew him, Thomas Hyde Hills will ever be held in grateful remembrance.

W. H.

By the death of CHARLES HEISCH the Society loses another of its original members. Charles Heisch was born at Blackheath on

August 2, 1820, and was the youngest son of Frederic Heisch, of Cox, Heisch, and Co., America Square, London.

In consequence of his early liking for scientific experiments, &c., he became, about the age of 15, a pupil of Richard Phillips, F.R.S., in his laboratory at St. Thomas's Hospital, and continued his studies with that chemist at the laboratory in Craig's Court, Charing Cross, then attached to the Geological Survey, which afterwards developed into the Royal School of Mines.

In 1842, Heisch was appointed Assistant Lecturer on Chemistry at St. Thomas's Hospital with Dr. Leeson; in 1848 he was elected joint Lecturer in Chemistry (with Mr. Thomas Taylor) at the Middlesex Hospital, and on the subsequent retirement of Mr. Taylor he became sole Lecturer in the subject until he resigned the chair in 1875. On March 11, 1869, he was elected Superintending Gas Examiner to the Corporation of the City of London, a post which he retained till his death, after a short illness, at Brighton, on January 2, 1892.

Heisch was present at the meeting on March 30, 1841, when it was determined to found the Chemical Society; he was also present at the Jubilee Dinner of the Society on February 25, 1891. He read a paper before this Society, "On the Quantitative Estimation of Cyanogen in Analysis," in 1849, and a second paper, "On the Organic Matter in Water," 1870, which contained an account of his well-known "sugar test." Among his other papers may be mentioned the following:—"On the Method of Testing the Illuminating Power of Gas, with special reference to Burners," read before the British Association of Gas Managers in 1870, and an important joint report to the Gas Institute by F. W. Hartley and C. Heisch, "On a Consistent Method of Estimating the Illuminating Power of Gas of Different Qualities," which provoked at the time much discussion. He also had a considerable share in starting the Society of Public Analysts, and was elected, at its foundation in 1874, joint Secretary with Mr. Wigner, a post which he filled until he was elected President in 1881 and 1882. He contributed many short papers to the *Analyst* on the melting point of fats, and on cocoa, milk, pepper, &c. He was Public Analyst to the district of Lewisham, St. John's, Hampstead, and the borough of Hertford.

Heisch was an accomplished musician, and at one portion of his life devoted much time to photography. He married in 1869, and leaves a widow, but no family. Those Fellows who had the pleasure of his acquaintance will long remember his fine presence, his courteous manner, and his characteristic laugh. J. F. M. P.

XLVI.—*Indications of a possible New Element in an Egyptian Mineral.*

By H. Droop Richmond, and Dr. Hussein Off, Khedivial Laboratory, Cairo.

His Excellency Johnson Pasha submitted to us, during 1890 and 1891, several specimens of a fibrous alum, found by him in geological investigations in little known parts of Egypt; deeming them of little interest at first, we put them aside in favour of other specimens from his numerous and valuable collection.

In the middle of 1891, we received from him a larger quantity of these alums, and examined them more closely, and in all detected cobalt, a hitherto unknown substance in Egypt, in quantities varying from 1·02 per cent. to 3·63 per cent. At the request of the holder of the concession from the Egyptian Government of the right to work the minerals in the district where they were found, we extracted a considerable quantity of cobalt from these alums, and in doing so observed a substance with whose properties we were not familiar.

We dissolved a considerable quantity (100 kilos.) of this alum in water, and added acetic acid and sodium acetate, and through this solution we passed sulphuretted hydrogen, when a white precipitate was thrown down; this was filtered off, and on passing more sulphuretted hydrogen, was succeeded by a black precipitate containing cobalt and iron sulphide; the white precipitate was well washed, extracted with dilute hydrochloric acid, then boiled with aqua regia, and the solution filtered and left to cool; a small quantity of calcium sulphate separated, and after it was removed, the solution was evaporated and taken up again with dilute hydrochloric acid, and precipitated by ammonia. The precipitate thus obtained was washed, dissolved in a small excess of sulphuric acid, and crystallised from 50 per cent. alcohol; a second crystallisation gave us a nearly white sulphate, and removed the bulk of the iron salts present; the sulphate was then dissolved in water, and precipitated by caustic soda, in which the whole of the precipitate except a little iron oxide was soluble; on precipitating the caustic soda solution by ammonium chloride, a white precipitate was obtained, which was dissolved in hydrochloric acid, and the treatment with caustic soda and ammonium chloride repeated.

This well-washed precipitate was then dissolved to saturation in hot dilute hydrochloric acid, and gave a solution acid to litmus, and absolutely neutral to methyl-orange.

We took three portions of 25 c.c. each, and one of 17·5 c.c., and precipitated with ammonia (α), sodium phosphate and ammonia (β), silver nitrate (γ), and ammonium oxalate (δ).

The weights of the precipitates were :—

α. 0·176 gram; calc. 0·059 gram.
β. 0·235 ,, ,, ,, ,,
γ. 0·354 ,, = 0·0851 gram Cl = 0·057 gram P_2O_5.
δ. 0·176 ,, leaving 0·103 gram or 58·5 per cent. on ignition = for 25 c.c. 0·147 gram.

These results show that an element of high molecular weight was present, and the practical agreement between the phosphoric acid calculated from two sources indicates that the precipitation was practically complete. The amount of substance obtained on igniting the precipitate with ammonium oxalate afforded evidence that we were dealing with a mixture.

We then precipitated a quantity of our solution with ammonium oxalate, washed the precipitate, and ignited it; the residue was dissolved without any great difficulty in hydrochloric acid, the solution neutralised and again precipitated with ammonium oxalate; precipitation was proved to be complete the second time; the first precipitation left a quantity of alumina in solution.

We dried the precipitate at 130° for four hours, and made the following determinations :—

(*a.*) 0·2015 gram left 0·115 gram (slightly grey) on ignition.
,, ,, ,, 0·113 ,, (white) on further ignition.
(*b.*) 0·1895 ,, gave 0·0529 ,, oxalic acid by titration.
(*c.*) 0·2125 ,, ,, 0·0586 ,, ,, ,,
(*d.*) 0·2965 ,, left 0·168 ,, on ignition (greyish).
(*e.*) 0·2405 ,, ,, 0·137 ,, ,, ,,
and gave 0·0755 ,, water.
(*f.*) 0·2695 gram left 0·154 ,, on ignition (greyish),
and gave 0·0825 ,, water.
(*g.*) 0·651 gram left 0·360 ,, on ignition (quite white),
and gave 0·208 ,, water.

These results gave the following percentages :—

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	Mean.
Residue on ignition, grey....	57·1	—	—	57·0	57·0	57·1	—	57·05
Residue on ignition, white...	56·1	—	—	—	—	—	55·3	55·70
Oxalic anhydride	—	15·95	15·75	—	—	—	—	15·85
Water.........	—	—	—	—	31·3	30·6	31·9	31·27
								102·87

From the mean of these figures we calculated (assuming that the residue is an oxide) an equivalent of 122, or 114 for the corresponding metal; if bivalent, the metal would have an atomic weight of 228.

The periodic law of Newlands and Mendeléeff predicts an element of atomic weight 225 in the family containing glucinum, calcium, strontium, and barium. The following list of reactions will show that it resembles glucinum in many of its properties, and calcium in its oxalate; analogies to zinc, which occurs in the other division of the same family, are also to be noted.

Reagent.	Reaction.
Caustic soda	White precipitate soluble in excess.
Ammonia	„ „ insoluble in excess.
Sulphuretted hydrogen	In an acid or neutral solution of the chloride, nothing; in an acetic solution, white, gelatinous precipitate after some time, the concentrated solution becoming nearly solid; the precipitate is easily soluble in hydrochloric acid, but insoluble in acetic acid.
Ammonium sulphide..	White, gelatinous precipitate, insoluble in excess.
Sodium sulphide	Do. do. do.
Ammonium carbonate .	White precipitate, insoluble in a hot concentrated solution.
Ferrocyanide of potash	White precipitate, soluble in an excess of the chloride, insoluble in an excess of the reagent.
Ferricyanide of potash	Nothing.
Potassium chromate...	Yellow precipitate, soluble in an excess of the chloride, insoluble in excess of the reagent.
Ammonium oxalate ...	White precipitate, soluble in an excess of the chloride, insoluble in excess of the reagent.
Potassium cyanide....	White precipitate, soluble in an excess of the chloride, insoluble in an excess of the precipitant.
Sodium potassium tartrate	White precipitate, soluble in excess; ammonia and caustic soda do not produce a precipitate in this solution.
Potassium sulphate ...	Added to a strong hot solution produced a white precipitate; the filtrate, after boiling the whole, did not crystallise on cooling; very little precipitate was

Reagent.	Reactions.
	obtained from it by the addition of ammonia, and no octahedrons or cubes were seen by a microscopic examination of the residue left on evaporation.
Sodium acetate	On heating, a white precipitate falls, which is completely redissolved on cooling the solution.

The oxide heated with cobalt nitrate gives a somewhat weak blue coloration.

The oxide, after ignition, increases in weight appreciably on exposure to the air, and is completely soluble in hydrochloric acid; the weight does not decrease by long heating in a current of hydrogen, but the oxide, as well as the oxalate, becomes a little darker under these conditions.

The attempts made to prepare the metal by reduction of the chloride by sodium, and by electrolysis of an alkaline tartaric solution, failed; an alkaline cyanide solution could not be prepared.

The solution of the chloride evaporated to dryness formed a nacreous mass, which does not adhere to the capsule, and is moistened with some difficulty by water, in which it is completely soluble even after a gentle ignition; this solution does not crystallise, but becomes a syrup when concentrated.

The sulphate is the only crystalline salt that we have prepared; it crystallises well from 50 per cent. alcohol, and may thus be fairly well separated from ferric sulphate.

As these properties do not accord with those of any known element, we propose to name this substance provisionally "masrium" from Masr (مصر), the Arabic name for Egypt, and the fibrous alum in which it was found "masrite."

The composition of the latter is as follows:—

		SO_3 required.	
Water	40·35		19·5 equiv.
Alumina	10·62	25·91	3·09
Ferric oxide	1·63	2·48	
"Masric" oxide	0·20	0·06	5·97
Manganous oxide....	2·56	2·89	
Cobaltous oxide	1·02	1·10	
Ferrous oxide.......	4·23	4·70	
Sulphuric anhydride .	36·78		4·00
Insoluble, clay, &c. ..	2·61		
	100·00		
Total iron as Fe_2O_3 =	6·33		

These numbers agree fairly well with the formula

$$(Al,Fe)_2O_3,(Ms,Mn,Co,Fe)O,4SO_3,20OH_2,$$

considering the difficulty of estimating water, and the exact state of the iron oxides. The water is not all driven off at the temperature at which the mineral begins to decompose and oxidise.

As the presence of cobalt in Egypt has not been noted before, we were curious to see if the ancient Egyptians had used it for colouring their monuments, "antiques," &c., but in the few specimens placed at our disposal by M. Grebaut, Director of the Guizeh Museum, we were unable to detect it; copper and iron were the colouring matters.

We reserve many points concerning this substance, and are continuing our work independently, and hope soon to elucidate the nature of this interesting mineral.

XLVII.—*Determination of the Temperature of Steam arising from Boiling Salt Solutions.*

By Jōji Sakurai, F.C.S., Professor of Chemistry, the Science College, Imperial University, Japan.

Introduction.

Although it is well known that the boiling point of a salt solution is always higher than that of water under the same pressure, the temperature of steam arising from such a solution has been the subject of much dispute, and, even at present, different opinions seem to prevail among chemists and physicists.

According to one set of observers, the temperature of steam arising from a boiling salt solution is the same or nearly the same as that of the solution: Gay-Lussac and Faraday, and, subsequently, Wüllner, Magnus, and Pfaundler, rank among these. According to the other, it is the same or nearly the same as that coming from pure water boiling under the same pressure, whatever may be the temperature of the boiling solution: this is the view held by Rudberg and, to a certain extent, by Müller. Experimental proofs are adduced on both sides, but these, as I shall show, are none of them conclusive, and establish, I think, neither the one view nor the other.

The determination of the real temperature of steam arising from a boiling salt solution presents many experimental difficulties; for, besides others to be mentioned later on, steam condenses upon the bulb of the thermometer and also upon the sides of the vessel above the vapour, unless special precautions be taken, so that the temperature indicated will not be higher than 100°. If, on the other hand, the walls of the containing vessel be maintained at a higher temperature, the thermometer will be exposed to the heat radiated from them, and will indicate a higher temperature.

For some time past, I have been engaged in an experimental investigation of the determination of the temperature of steam escaping from boiling salt solutions, and have devised a method which is, as far as I can see, free from such objections. By this means, it can be readily shown that the temperature of the steam escaping from the boiling salt solution is exactly the same as that of the solution itself.

Before proceeding, however, to a description of my own experiments, I shall briefly refer to the history of this question, discussing the methods employed and the results obtained by previous workers.

Historical Summary and Short Critical Review of the Work already done.

Faraday, as long ago as 1822, published the results of his experiments upon this question in the *Annales de Chimie et de Physique* for that year. He found that when the bulb of a thermometer was sprinkled over with a salt and then introduced into steam coming out of boiling water, the thermometer showed a temperature higher than 100°, especially when it was held horizontally, so as to prevent the salt from being washed away too quickly. Still higher temperatures were observed by him when, the experiment being otherwise the same, the thermometer bulb was wrapped up in a linen or woollen cloth. From these experiments, Faraday concluded that since a salt solution was heated up to its boiling point by the action of steam at 100° upon the salt, therefore the steam generated from a boiling salt solution had only the temperature of 100°.

Gay-Lussac, as the editor of the French journal, appended a note to this paper, in which he first pointed out that facts similar to those observed by Faraday had long been known in France, namely, that when steam from boiling pure water was passed into a cold concentrated solution of a salt, the latter could be heated up nearly to its boiling point. Then, with regard to Faraday's view that steam generated from a boiling salt solution has only the temperature of 100°, Gay-Lussac remarked: "Sans invoquer ici le secours de la théorie, nous pouvons affirmer, d'après le témoignage irrécusable de l'expérience, que la temperature de la vapeur fournie par un liquide quelconque, sous une pression quelconque, est exactement celle de la couche liquide immédiatement en contact avec la vapeur."

Faraday then undertook more researches on this question, and in the *Quarterly Journal of Science* for 1823, he published the results of his experiments, and stated that he had proved Gay-Lussac's assertions to be correct, but that he had been astonished at the difficulty of obtaining definite results. Only when he used a double-walled vessel, which contained the experimental solution both between the walls and also above them, only when he heated the thermometer previously to a temperature higher than that of the boiling solution, and only after repeated observations, had he been able to convince himself that no anomaly existed in this phenomenon. These experiments of Faraday will be criticised presently along with those of Magnus.

Rudberg (*Ann. Chem. Phys.* [*Pogg.*], **34**, 257), in 1835, published the results of a long series of observations on the temperature of steam evolved from different solutions, boiling under different pressures, and pointed out that it is always the same as that of steam arising from pure water boiling under the same pressure. Some of his numbers are quoted below.

	Temperature of steam.		
Pressure in mm.	Water.	Salt solution.	Salt.
761·54	100·06°	100·07°	$Ca(NO_3)_2$
763·37	100·12	100·13	,,
769·64	100·35	100·34	,,
769·17	100·33	100·36	KNO_3
773·20	100·49	100·50	,,

The experiments of Rudberg are always regarded as conclusive evidence that the temperature of steam issuing from a boiling salt solution is only 100°; but as they were carried out in the ordinary way without proper precautions against the steam cooling before reaching the thermometer, we must regard his results as unsatisfactory, in presence of the fact that with such precautions the temperature proves to be higher.

Wüllner (*Ann. Chem. Phys.*, **110**, 387), from determinations of the tension of steam arising from boiling salt solutions, pointed out that such steam, having less tension than that evolved from pure water at the same temperature, must be non-saturated, and that theoretically, therefore, it could not have the temperature of 100°.

Magnus (*Ann. Chem. Phys.*, **112**, 408) is generally regarded as having experimentally proved that steam from a boiling salt solution has a temperature equal, or nearly equal, to that of the solution itself. It will, therefore, be interesting to know exactly the nature of his evidence, and I propose to refer to his paper somewhat in detail. In the first part, Magnus mentions that Rudorff, who was working in his laboratory, had devised two methods of ascertaining the real temperature of steam coming out of a salt solution, the results showing that the temperature of the steam is above 100°.

One of these methods consists in dipping the thermometer into a boiling salt solution and, when it has attained the temperature of the latter, in holding it in the steam over the solution. This method of ascertaining the temperature of steam is, as Magnus himself allows, by no means convincing; for, as already observed by Faraday and others, when such a thermometer is held in the steam arising from boiling pure water, temperatures higher than 100° are always indicated.

The other method consists in previously heating the bulb of a thermometer to a temperature higher than that of the boiling solution, and then introducing it into the steam. It is said that, in this way, temperatures approaching the boiling point of the solution are indicated. I have, however, repeatedly tried this method, and have fully convinced myself that if sufficient care is taken to protect the bulb of the thermometer against the splashing up of the hot solution, the temperature rapidly falls to 100°.

After referring to these two methods proposed by Rudorff, and after giving a good historical summary of the subject, to which I am greatly indebted for this part of my paper, Magnus goes on to describe his own method and the results obtained by its means. His apparatus consists of a double-walled metallic vessel, filled to a convenient height, both within and without the inner walls, with the experimental solution. Steam, generated by heating the solution from below, rises in the inner as well as in the outer chamber, and escapes by means of a lateral tube, also metallic and provided with two holes, one of which opens into the inner chamber and the other into the outer chamber. The object of having double chambers is to keep the inner one surrounded by hot steam; so as to prevent loss of heat by radiation. The temperature of the steam is indicated by means of a thermometer held horizontally and inserted in the lateral tube, its bulb being placed in the centre of the inner chamber. The following are the results obtained by Magnus with a solution of calcium chloride.

Temperature		
Of the solution.	Of the steam.	Difference.
107·0°	105·25°	1·75°
107·5	105·5	2·00
108·0	105·8	2·2
109·2	106·5	2·7
110·0	107·0	3·0
111·0	107·6	3·4
112·0	108·1	3·9
113·0	108·8	4·2
114·0	110·0	4·0
115·0	110·9	4·1
116·0	111·2	4·8

Magnus confesses that these numbers have no absolute value ; but, at the same time, he regards it as proved that the temperature of the steam is nearly the same as that of the solution, the difference being due to the unavoidable loss of heat by radiation. Such is the conclusion Magnus has drawn from his experimental results, and this seems to have been accepted by chemists and physicists as being convincing. Even those who had held the opposite view seem never to have criticised the method Magnus employed, or the results he obtained.

It seems to me, however, that the conclusion he draws from the results of the experiments is open to criticism. As the double-walled vessel, which he employed, was made entirely of metal, its walls must have been heated up by conduction nearly to the temperature of the boiling solution it contained, and the steam enclosed by such walls must have had nearly the temperature of the latter ; that is, a temperature more or less approaching that of the solution, and that quite independently of its temperature when generated. His numbers in the second column of the table may have indicated, therefore, not so much the temperature of the natural steam as that of the surrounding walls and of the steam superheated by them. Strange to say, Magnus seems to have been aware of this element of uncertainty in his results, and yet to have disregarded it. He writes :—" Soviel ist indess durch diese Versuche bewiesen, dass die Dämpfe, welche aus kochenden Salzlösungen aufsteigen, eine höhere Temperatur als 100° haben, und eine um so höhere, je höher die Temperatur der kochenden Lösung ist. Dass sie aber dieselbe Temperatur wie diese Lösung haben, ist mir nicht gelungen nachzuweisen, und ich zweifle dass diess möglich sein wird. Denn wenn die Wände des Dampfraumes auf der Temperatur der kochenden Lösung erhalten werden, so ist man, wie schon oben bemerkt, nicht sicher, dass nicht die

Erwärmung von diesen Wänden hervorgebracht ist, haben dagegen die Wände eine niedrigere Temperatur, so wird auch die Temperatur des Thermometers niedriger ausfallen."

What then, it may pertinently be asked, is the value of his experimental results? It seems to me that Magnus erred in having the walls of his vessel of a highly conducting material, so that the thermometer would indicate the temperature of these walls, derived as it was from the solution and even from the heat of the lamp, and then to regard the temperature observed as being that of the steam. In fact, it can be readily shown that by keeping the walls of a vessel at a temperature higher than 100°, say at 110°, the steam issuing from water itself indicates a temperature almost equal to that of the walls.

The results obtained by Magnus, which have been regarded as the most weighty and conclusive experimental proof of the view that the steam arising from a boiling salt solution has the same or nearly the same temperature as the latter, thus appear to me to be valueless, and the same remark applies to Faraday's later experiments already referred to, in which he employed a double-walled vessel containing the experimental salt solution in both chambers.

Müller (*Ber.*, **9**, 1629), apparently not acquainted with Faraday's earlier experiments, made observations similar to his, and came to the same conclusion as Faraday first did, namely, that the steam generated from a boiling salt solution has only the temperature of 100°. He regards this view as being confirmed by the following considerations.

1st. The solution begins to boil (that is, steam bubbles freely rise to the surface and there burst) below its proper boiling point, and the temperature then slowly rises. The steam formed at first at 100° acts on the solution in the same manner as that passed from without, and heats it up to the boiling point.

2nd. Higher temperatures are indicated by salt solutions when boiling gently than when boiling violently; in the latter case, more steam bubbles coming in contact with the bulb of the thermometer. Similarly, a rise of temperature is observed on removing the flame after violent ebullition.

Müller's account of the first effect of heating a salt solution is so remarkable that I feel it incumbent to adhere closely to his words. He says: "A solution of calcium chloride whose boiling point is 126°, for example, is already completely boiling at 110°, and the temperature then rises to 126° in about half a minute" (*loc. cit.*, 1631). I have repeatedly tried similar experiments, but have never been able to confirm the statement that the solution, whose proper boiling point is 126°, *is completely boiling* at 110°, though it is perfectly true that the solution *begins to boil* at about this temperature.

I confess, therefore, that it is a relief to me to be able to dispense with any discussion of Müller's interpretation of these phenomena, for whatever their signification may be, the fact that the observed phenomena of *incipient* ebullition of a salt solution differ in no respect from those of pure water, except that of higher temperatures, deprives them of all value for throwing light upon the question at issue. A similar remark may be made with regard to Müller's other observations, namely, those which relate to the difference of temperature in the boiling solution, according as it is freely evolving the steam or not. It is a well-known fact that a thermometer dipped into a boiling liquid, say water, gives very irregular indications, higher temperatures being always indicated when steam is less freely escaping. In short, the facts observed by Müller are by no means limited to salt solutions, and his argument that the steam at the moment of its formation has only the temperature of 100° cannot, therefore, be regarded as in any degree satisfactory.

Wüllner (*Ber.*, **10**, 256) wrote a note on Müller's paper, pointing out that the fact that a solution of calcium chloride may be heated up to its boiling point by the action of ordinary steam had already been known to Gay-Lussac and observed by Faraday, who on more careful experimental enquiry changed his first opinion, and came to the conclusion that the steam escaping from a boiling salt solution must have the temperature of the latter. He also points out again that such steam is not saturated, and that, therefore, it could not have the temperature of 100°.

Pfaundler (*Ber.*, **10**, 463) objects to Müller's conclusion on much the same grounds as Wüllner, and fully supports the views of the latter. Further on, Pfaundler attempts to explain the fact observed by Magnus that the temperature of steam arising from a boiling salt solution is not quite the same as that of the latter; this explanation, which is not easy to accept, is also not needed, as the facts observed by Magnus, and upon which this explanation is based, are, as already pointed out, by no means convincing. My own experiments prove, moreover, that there exists no difference between the temperature of the boiling solution and that of the steam issuing from it.

The above summary should give some idea of the vagueness and unsatisfactory character of the experimental evidence now existing as regards the temperature of the steam arising from a boiling salt solution. The following is a description of my own experimental methods, and the results obtained by their means.

Experimental Methods.

For success in establishing the true temperature of the steam escaping from boiling salt solutions, certain conditions must be observed.

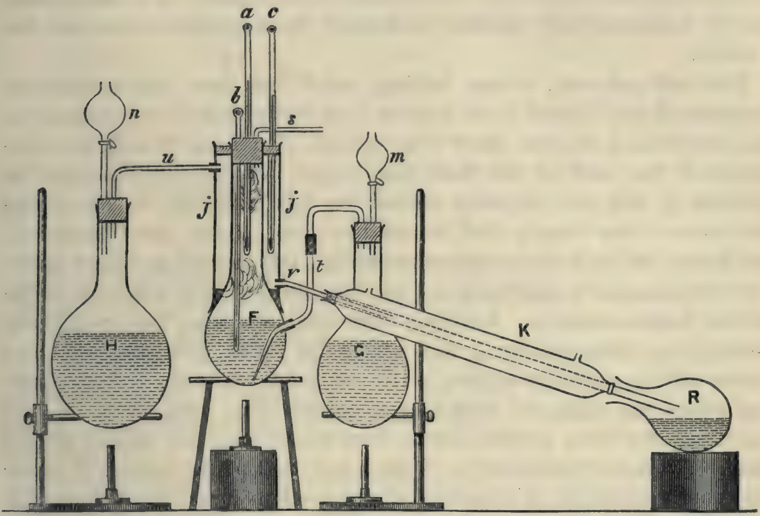
1. The thermometer must be kept clear of all contact with the solution, even the smallest drops thrown up by ebullition, as otherwise it is evident that the experiment loses all claim to accuracy.

2. The effect of the radiant cooling of the thermometer must either be prevented, or rendered inappreciable in proportion to the heating up by the steam. Before considering these alternative conditions, it may be well to call attention to the familiar and striking evidence we have that loss of heat by radiation from the bulb of the thermometer does occur and cannot be neglected. Whenever distillation of water, or any other liquid with no fixed matters dissolved in it, is going on, the thermometer immersed in the vapour to record the "boiling point" is seen to be always condensing some of the vapour, drops falling from it into the boiling liquid.

The former alternative seems hardly practicable, or, at least, has proved to be impracticable under various conditions in my hands. The latter alternative, that of overpowering the loss of heat by radiation by rapid removal of the vapour in contact with the thermometer, can be easily effected by the expedient of combining the introduction of steam from without with the boiling of the solution by the lamp, the combination being regulated by maintaining steady the temperature marked by the thermometer in the solution. Ebullition alone should suffice for this purpose, but the practical difficulties in the way render it insufficient. The boiling would have to be tumultuous to generate much vapour, and in a short time the solution would become too concentrated for the experiment to be continued with convenience. On the other hand, with due regulation of the steam entering from without and the height of the flame, an abundant supply of steam can be got without impediment. Moreover, irregular boiling and bumping of the solution are both entirely prevented when the operation is worked in this manner.

3. The walls of that part of the vessel which serves as the steam chamber for the thermometer must be sufficiently protected from cooling externally, and yet, at the same time, not be heated to the temperature of the steam. For if, as in Rudberg's experiments, the former condition is not observed, so much of the steam is condensed in keeping the walls at 100° that it is hardly possible to keep enough passing over the thermometer bulb; while if the latter condition is ignored, as in Magnus's experiments, the indications of the thermometer may be illusory.

The arrangement which I adopted after several trials and modifications in order to meet these conditions was as follows. It consisted of an elongated, round-bottomed flask, F, with a long neck; this flask contained the experimental salt solution. The mouth of the flask was provided with a cork, through which passed two thermometers, *a* and *b*, and a tube *s* for the escape of steam; the thermometer *a* was used to indicate the temperature of the steam, and the thermometer *b* that of the solution. The neck and a part of the flask F was enclosed in a glass cylinder, *jj*, fixed above by means of a cork and below by means of an india-rubber band. Through the cork of the cylinder, and by the side of the neck of the flask F, passed a third thermometer, *c*, whose bulb was kept at the same height as that of the steam thermometer *a*. The body of the flask, finally, was provided with a hole in its side, through which a glass tube, *t*, somewhat drawn out at one of its ends and bent as shown in the figure, was passed and jointed to the flask by means of a short piece of india-rubber tubing slipping over it. This tube, whose drawn-out end nearly reached the bottom of the flask, was used for supplying steam from the boiler G. The glass cylinder *jj* was connected on one hand with another flask, H, and on the other with a condenser, K; these connections were made as before by means of short pieces of india-rubber tubing slipped on over the glass tubes *u* and *v* respectively. The flask H contained acetic acid somewhat diluted with water. The flasks F, G, and H were supported on stands, and F rested on a piece of asbestos cardboard, having a hole in the centre, so that only the bottom might be heated by the direct flame. The stoppered funnels *m* and *n* served to supply the flasks G and H with water and



acetic acid respectively, when necessary, without dismounting the apparatus. The funnel *m* further served, at the end of an experiment, to restore the equilibrium of pressure between the outer air and the inside of the flask G, thus preventing the salt solution from being sucked into the latter. The whole arrangement is exceedingly simple, and can be fitted up by any one with materials found in every chemical laboratory. The three thermometers *a*, *b*, and *c* had, finally, been carefully verified, including the exposure correction for *a* and *c*.

The salt solution, whose boiling point had been approximately determined and known to be higher than that of the dilute acetic acid, was introduced into the flask F by means of a long funnel, and the inside of the neck of the flask then wiped with a cloth, so that no particle of the salt solution should be left adhering to it. Some cotton-wool was loosely tied round the stem of the thermometer *b*, and below the bulb of the thermometer *a*; this served as a very effective screen against splashing up of the solution on to the bulb of the second thermometer *a*. A little cotton wool was also tied round the stem of the thermometer *a*, and above its bulb; this prevented any water which might condense in the steam-issue tube *s*, from flowing down the stem of this thermometer. The cork with its two thermometers thus prepared was then fitted into the mouth of the flask F; this cork projected a little below that of the jacket, in order that there might be no chance of steam condensing within the neck of the flask. The tubes *u* and *t* were covered with cotton-wool in order to lessen the cooling action of the air on the acetic acid vapour and the steam respectively.

The acetic acid was now made to boil in the flask H. Its vapour, passing into the jacket *jj*, heated up the walls of the neck of the flask, that is, of the steam chamber over the solution, then passed into the condenser K, and collected in the receiver R. The flame under the flask H was so regulated that the acetic acid only slowly distilled; in this manner, a steady supply of vapour of almost constant temperature could be readily maintained in the jacket. The thermometer *c* rapidly rose to about 111° under the influence of the acetic acid vapour, whilst the thermometer *a* more slowly rose, until ultimately it also showed about the same temperature.

The salt solution was next heated to boiling. The water in the flask G, which had been kept nearly boiling, was then also made to boil regularly, and a rapid current of steam was passed into the salt solution boiling in the flask F. The thermometer *a* now began to rise above that in the jacket, until it indicated the same temperature as that of the solution. The flame under the boiling solution was so regulated that the temperature of the latter should either remain constant or rise very slowly. The results obtained in one experiment with a solution of calcium chloride are shown below.

Temperature of the			Difference.	
Steam. (I.)	Solution. (II.)	Acetic acid vapour. (III.)	(II.) – (I.)	(I.) – (III.)
111·2°	112·5°	110·8°	1·3	0·4
111·7	112·5	110·9	0·8	0·8
112·2	112·6	111·1	0·4	1·1
112·5	112·7	111·3	0·2	1·2
112·7	112·9	111·5	0·2	1·2
113·0	113·0	111·6	0·0	1·4
113·1	113·2	111·8	0·1	1·3
113·3	113·3	111·9	0·0	1·4

The time occupied was about 20 minutes. The bulb of the steam thermometer *a* remained perfectly clean; indeed, by washing it with a little water and adding a drop of silver nitrate solution to the washings, not a trace of cloudiness was produced, showing that the splashing of the solution on to it had been completely prevented. In fact, the upper portion of the cotton-wool remained perfectly clean and dry.

For the following two experiments, still more dilute acetic acid was employed. The results obtained with a solution of sodium nitrate are as follows :—

Temperature of the			Difference.	
Steam. (I.)	Solution. (II.)	Acetic acid vapour. (III.)	(II.) – (I.)	(I.) – (III.)
106·6°	107·5°	105·9°	0·9	0·7
106·9	107·6	105·9	0·7	1·0
107·2	107·6	106·0	0·4	1·2
107·5	107·7	106·1	0·2	1·4
107·7	107·8	106·2	0·1	1·5
107·7	107·8	106·2	0·1	1·5
107·8	107·8	106·3	0·0	1·5

The time occupied was again about 20 minutes. The following are the observations made with a solution of potassium nitrate :—

Temperature of the			Difference.	
Steam. (I.)	Solution. (II.)	Acetic acid vapour. (III.)	(II.) – (I.)	(I.) – (III.).
107·8°	109·4°	107·8°	1·6	0·0
108·3	109·5	107·8	1·2	0·5
108·7	109·7	108·0	1·0	0·7
109·1	109·8	108·1	0·7	1·0
109·3	109·8	108·2	0·5	1·1
109·5	109·9	108·2	0·4	1·3
109·8	110·0	108·2	0·2	1·6
110·0	110·2	108·3	0·2	1·7
110·2	110·3	108·4	0·1	1·8
110·2	110·3	108·5	0·1	1·7

The time occupied was about half an hour.

In the following experiment a stronger solution of calcium chloride was taken, and amyl alcohol (containing a little of the lower alcohols) was employed instead of acetic acid.

Temperature of the			Difference.	
Steam. (I.)	Solution. (II.)	Amyl alcohol vapour. (III.)	(II.) – (I.)	(I.) – (III.)
127·5°	128·3°	126·5°	0·8	1·0
128·1	128·5	126·8	0·4	1·3
128·6	128·9	127·2	0·3	1·4
129·1	129·2	127·8	0·1	1·3
129·4	129·5	128·1	0·1	1·3
129·7	129·8	128·3	0·1	1·4
129·8	129·8	128·5	0·0	1·3

The time occupied was about 20 minutes.

The experiments above described prove, beyond any possible doubt, that *the temperature of the steam escaping from a boiling salt solution is exactly the same as that of the solution.* This, I believe, is the first occasion on which the above important fact has been experimentally established. Philosophers had, indeed, asserted that the temperature of such steam should be, or would be, the same as that of the solution, but without any experimental proof. Gay-Lussac's assertion, "the temperature of the vapour furnished by any liquid is exactly the same as that of the liquid layer in immediate contact with the vapour," is based upon the knowledge of the facts derived from the study of simple liquids, such as water, alcohol, &c.; for no direct experiments had been made by him, or any other investigator before him, upon the temperature of the steam arising from a boiling *salt* *solution* which established the truth of that assertion. So far as direct experimental evidence is concerned, he had, I think, no good reason for extending his remarks to the case of a salt solution. Faraday thought he had proved Gay-Lussac's assertion to be correct in the case of salt solutions also, but upon evidence not at all convincing. Magnus could not show that the temperature of the steam is exactly the same as that of the solution. "That, however, it (the steam) possesses the same temperature as the solution I cannot prove, and I doubt whether it can possibly be proved," he says. The grounds for such doubt have now been removed by the experiments above described, the secret of the success lying in the fact that *the walls of the steam-chamber must be above* 100°, *and yet below the temperature of the solution, and that, at the same time, a sufficient quantity of steam must escape from the solution to ensure that these walls shall have no material cooling effect upon the steam.* To meet this condition the quantity of steam evolved from the boiling solution itself is not sufficient, and hence the necessity of passing steam from without into the boiling solution.

That the quantity of steam merely arising from a boiling salt solution is not sufficient to overcome the cooling effect of the walls will best be seen from the following numbers. These refer to a solution of calcium chloride experimented upon in exactly the same manner as before, but without introduction of steam from an external source. The acetic acid was also more rapidly distilled.

Temperature of the			Difference.	
Steam. (I.)	Solution. (II.)	Acetic acid vapour. (III.)	(II.) – (I.)	(III.) – (I.)
103·0°	111·9°	103·2°	8·9	0·2
103·4	114·4	103·5	11·0	0·1
103·7	115·2	103·7	11·5	0·0
104·1	117·0	104·2	13·0	0·1
104·5	118·4	104·5	13·9	0·0
104·8	120·5	105·1	15·7	0·3
104·9	122·6	105·3	17·7	0·4
105·1	125·2	105·5	20·1	0·4

In spite of the fact that the solution was boiling briskly with a free and uninterrupted evolution of steam, and in spite of the additional fact that the temperature of the boiling solution rose from 111·9° to 125·2°, the temperature of the steam only rose from 103° to 105·1°, and never above that of the acetic acid vapour in the jacket. The rise that did occur is evidently due to the heating effect of the acetic acid vapour; for, in this case, the outer surface of the steam-chamber was constantly wet, owing to the condensation of the acetic acid vapour upon it. Acetic acid vapour, and not steam, was then acting as the heater.

This result was so remarkable and apparently so conclusive, that I was for some time induced to believe that the temperature of the steam escaping from a solution of calcium chloride boiling at the temperature of even 125° is lower than 105° and probably only 100°. By slightly modifying the experiment, namely, by keeping the distillation of the acetic acid at a very slow rate, while the solution was kept boiling as briskly as possible, the steam-thermometer could be made to indicate somewhat higher temperatures than the acetic acid vapour, but far below the temperature of the solution. It was this observation, however, that led me to try the introduction of steam into the solution from without.

By the introduction of steam into the boiling solution from without, evaporation and condensation of steam in the solution can be so readily and exactly counterbalanced, that its boiling temperature may be maintained constant for any length of time and within a few thousandths of a degree Centigrade. I am developing this part of my observation for the exact determination of the boiling points of various solutions, and also for simplifying the determination of molecular weights by the boiling method, which has, of late, been made the subject of an extensive study by Beckmann.

In conclusion I wish to express my warmest thanks to my colleague Dr. E. Divers, F.R.S., for many valuable criticisms and suggestions from time to time while this investigation was in progress, and also to Dr. C. G. Knott and Professor K. Yamakawa for the interest which they have taken in my work.

XLVIII.—*Chemistry of the Compounds of Thiourea and Thiocarbimides with Aldehyde-ammonias.*

By Augustus E. Dixon, M.D., Professor of Chemistry, Queen's College, Cork.

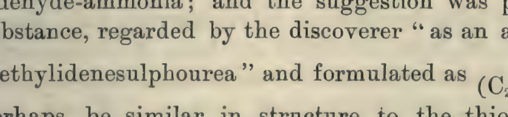
Some years ago (Trans., 1888, 411), I laid before this Society an account of the interaction of the "mustard oils" with the aldehyde-ammonias, in which it was shown that the action is a generic one, at least for the thiocarbimides containing univalent hydrocarbon residues. Thus, it was found that, under similar conditions, 1 mol. of ethyl-, allyl-, phenyl-, benzyl-, and orthotolyl-thiocarbimides, respectively, combine with 2 mols. of acetaldehyde-ammonia, with elimination of both the oxygen atoms of the latter, in the form of water. Further, it was shown that phenyl- and benzyl-thiocarbimides combine readily with isovaleraldehyde-ammonia, yielding similar products.

The equations representing these interactions were provisionally formulated, thus:—

$$CSNR + 2CH_3{\cdot}CH{<}^{OH}_{NH_2} = CS{<}^{NR\cdot CH(CH_3)}_{NR\cdot CH(CH_3)}{>}NH + 2H_2O,$$

the valeraldehyde derivatives being considered as similar in type, namely, $CS{<}^{NR\cdot CH(C_4H_9)}_{NH\cdot CH(C_4H_9)}{>}NH$.

In this connection, attention was drawn to a compound obtained by Nencki (*Ber.*, **7**, 162) from the interaction of thiourea itself with aldehyde-ammonia; and the suggestion was put forward that this substance, regarded by the discoverer "as an ammonia compound of diethylidenesulphourea" and formulated as $\left.\begin{matrix}CS\\(C_2H_4)_2\end{matrix}\right\}N_2,NH_3$, might, perhaps, be similar in structure to the thiocarbimide derivatives already mentioned: representing, in fact, the parent type, of which the latter are the substitution products. On this view, the formation of the compound was provisionally explained as follows:—



$$CS{<}^{NH\,H}_{HN\,H} + \begin{matrix}OH\ CH(CH_3)\\OH\ CH(CH_3)\end{matrix}\begin{matrix}NH\,H\\NH_2\end{matrix} =$$

$$CS{<}^{NH\cdot CH(CH_3)}_{NH\cdot CH(CH_3)}{>}NH + NH_3 + 2H_2O.$$

The object of the present investigation was to endeavour to acquire some further knowledge of the chemistry of these substances, with a view, first, to ascertain whether Nencki's and the thiocarbimide compounds are really members of the same class; secondly, to gain, if possible, some information regarding their structure; and, thirdly, to learn whether the process of their formation can be extended to other varieties of thiocarbimides and aldehydes. Advantage has been taken of the opportunity to prepare the methyl derivative of the thiocarbimide series, and a homologue of Nencki's compound has been obtained. The experimental results are detailed below.

Thiourea and Aldehyde-ammonia.

Nencki (*loc. cit.*) obtained the compound by boiling an aqueous solution containing 2 mol. proportions of aldehyde-ammonia to 1 of the amide. Boiling water, however, so readily decomposes the product that the yield by this method always falls considerably below the theoretical. But if the aldehyde-ammonia, dissolved in cold or tepid water, be added to the thiourea solution near its boiling point, the addition of some crystals of the ready-formed compound, prepared by boiling a few drops of the mixture in a test-tube, at once determines the separation of a considerable quantity of the substance, though the temperature of the mixture be comparatively low. The liquid is now rapidly cooled, and the crystals removed by filtration; on boiling the filtrate, a second crop is obtained. By this means, the yield amounts to about 85 per cent. of the theoretical.

In its ready decomposability into its constituents on boiling the solution,* this substance resembles the thiocarbimide compounds; the latter can only be recrystallised with heavy loss, even from alcohol. The substance is, as Nencki states, very sparingly soluble in alcohol; it is practically insoluble in ether, benzene, and chloroform. 180°, the melting point recorded by him, is substantially correct; according to my experiments, the substance, when carefully purified by repeated recrystallisation, melts between 183° and 184° (uncorr.) to a deep, bromine-coloured liquid, which immediately decomposes with evolution of gas.

Picrate.—A compound with picric acid was obtained by mixing an alcoholic solution of it with a warm aqueous solution of the base. Fine, hair-like needles separated on cooling, which, on recrystallisation from hot water, were obtained in lemon-yellow prisms, several centimeters in length. This salt does not melt at 230°, but, when heated over a gas flame, it darkens and decomposes, melting quietly, at a high temperature, to a blackish liquid with evolution of gas.

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* 100 parts (14 grams) of the compound, almost pure, gave on recrystallisation from boiling water only 42 parts.

A portion, dried over sulphuric acid, gave the following results on analysis:—

0·1937 gram of substance, burnt with copper oxide, gave 37·9 c.c. nitrogen, measured at 17° and 748·6 mm.

	Calculated for $C_5H_{11}N_3S,C_6H_2(NO_2)_3{\cdot}OH$.	Experiment.
N	22·51 per cent.	22·49 per cent.

Action of Silver Nitrate.—Equimolecular proportions of base and silver nitrate were mixed in cold aqueous solution. A bulky, white precipitate at once appeared, consisting of delicate, flexible, silky needles; it is very unstable, soon losing its lustrous appearance and becoming dark-coloured, even though the solutions be cooled to near the freezing point. It was drained on the filter-pump, rapidly washed with water, and dried over sulphuric acid.

As the filtrate was not acid to test-paper, it seemed unlikely that a silver substitution derivative was in hand. The substance was, in fact, easily shown to be an addition product, by boiling a portion with water and filtering from the silver sulphide thereby produced; the filtrate gave the reaction of nitric acid at once.

On analysis, the following data were obtained:—

0·4727 gram of substance, oxidised with nitric acid, yielded 0·2111 gram AgCl.

	Calculated for $C_5H_{11}N_3S,AgNO_3$.	Experiment.
Ag	34·24 per cent.	33·61 per cent.

A similar preparation was next made, using 2 mol. proportions of silver nitrate (alcoholic) to 1 of the aldehyde-ammonia compound. A silver determination gave the following result:—

0·3492 gram of substance, oxidised with nitric acid, yielded 0·1532 gram AgCl, or Ag = 33·02 per cent.

From this it follows that the compound $C_5H_{11}N_3S,2AgNO_3$, which would require 44·49 per cent. of silver, has not been produced; but the compound (which could not be obtained quite pure) is identical with the preceding.

Action of Water upon the Silver Compound.—The nature of this action was next investigated. When placed in contact with cold water, the silver compound soon begins to darken, and in a short time the mixture becomes black. If warmed with water, the decomposition sets in at once; aldehyde—easily recognised by its odour—is evolved, and a brilliant speculum of silver sulphide is formed on the sides of the tube.

Since the molecule contains but one atom of silver to one of sulphur, the decomposition by water can only* involve elimination of half the sulphur in combination with the metal. The filtrate from the sulphide, after previous boiling until aldehyde ceases to be evolved, does, in fact, contain sulphur in solution; thus, it gives a black precipitate with ammoniacal silver nitrate, and is readily desulphurised by warming with alkaline solution of lead. These reactions suggest the presence of thiourea, as a product of the partial desulphurisation: the latter was recognised in another portion of the filtrate by Claus' method (*Annalen*, **179**, 129), namely, after treating with ethylic nitrite, ferric chloride produces an intense blood-red coloration, due (according to Claus) to the conversion of the thiourea into ammonium thiocyanate. These facts may be represented by the following equation:—

$$2C_5H_{11}N_3S,AgNO_3 + 5H_2O = Ag_2S + 4CH_3{\cdot}CHO + CSN_2H_4 \\ + CO(NH_2)_2 + 2NH_4{\cdot}NO_3.$$

Action of Acetic Anhydride.—It has been shown by R. Schiff (*Ber.*, **9**, 570) that warm acetic anhydride readily acts upon the compound of phenylthiocarbamide with aldehyde-ammonia, thereby producing acetylphenylthiourea. Further on, it will be shown that a similar reaction holds in the case of the tolylthiocarbimide aldehyde-ammonia compound. The question therefore arose, whether, under like conditions, the aldehyde groups would be split off from Nencki's thiourea derivative, or whether, on the other hand, it would simply undergo acetylation.

To ascertain this, 10 grams (1 mol.) of the substance, dried by standing over sulphuric acid, were added to acetic anhydride (rather more than 2 mols.) contained in a flask provided with a bent delivery tube; the pasty mixture, on warming, began to turn red in spots, and, on further raising the temperature, a vigorous action commenced, which the heat evolved was sufficient to complete. Gas came off freely with effervescence, and the solid rapidly dissolved forming a deep brownish-red solution.

By means of the bent delivery tube, the gas was led into water; the aqueous solution thus obtained, when treated with a few drops of ammonia and boiled with ammoniacal silver nitrate, freely reduced the latter, thus showing the presence of aldehyde, and therefore indicating disruption of the molecule.

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* Unless hydrogen sulphide be liberated. In this case, as also in that of the homologue next to be described, not a trace of hydrogen sulphide was evolved.

The contents of the flask were now mixed with water; a quantity of blackish-brown, sticky oil separated, which was removed by filtration, and the brown-red filtrate twice treated with animal charcoal. A golden-yellow solution was thus obtained, which was evaporated to dryness and extracted with boiling ether. The residue left after the evaporation of the latter was dissolved in hot water, and the solution filtered; on cooling, well-formed, almost white, rhombic prisms separated, melting at about 163°. In appearance and melting point, this compound resembled acetylthiourea (m. p. 165°, Nencki and Leppert, *Ber.*, **6**, 905), and this was confirmed by the result of a nitrogen determination.

0·2126 gram of substance, burnt with copper oxide, gave 43·7 c.c. nitrogen, measured at 16·5° and 758·8 mm.

	Calculated for $CSN_2H_3 \cdot CO \cdot CH_3$.	Experiment.
N	23·77 per cent.	23·86 per cent.

Under the action of acetic anhydride, therefore, Nencki's compound behaves like thiocarbimide derivatives of aldehyde-ammonia, the aldehyde groups being split off as such, together with one of the three nitrogen atoms, whilst an acetylated thiourea is left. The action may be thus represented—

$$C_5H_{11}N_3S + (CH_3 \cdot CO)_2O + 2H_2O = CSN_2H_3 \cdot CO \cdot CH_3 + 2CH_3 \cdot COH + CH_3 \cdot COONH_4,$$

but it is by no means quantitative; much decomposition occurs, and tarry-looking substances are produced, the separation of which is accompanied by heavy loss of the acetylated thiourea.

Acetylthiourea very readily parts with its sulphur; cold silver nitrate produces a white precipitate, which blackens gradually on standing, or instantly on the addition of ammonia. It is also easily desulphurised by warming with alkaline lead solution, with production of a brilliant galena speculum.

Thiourea and Isovaleraldehyde-ammonia.

The generality of the interaction between the thiocarbimides and aldehyde-ammonias having been established within the limits stated above, it remained now to be learned whether the thiourea reaction could be extended.

Isovaleraldehyde-ammonia was selected for experiment.

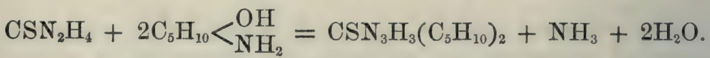
Thiourea (1 mol.), dissolved in boiling concentrated alcohol, was added to an alcoholic solution of the aldehyde-ammonia obtained from isovaleraldehyde (2 mols.). On heating the mixture to near its boiling point, ammonia was freely evolved; the solution was now let cool, and the solvent allowed to evaporate at the ordinary temperature. The residue, when collected and recrystallised from alcohol, yielded fine, large, glass-clear, rhombic plates which were practically pure (about 52 per cent. of the theoretical). The mother liquors, when poured into water, gave a further crop of the crude substance.

A portion of the first crop was further purified by precipitating the alcoholic solution with water, washing the precipitate well with ether, and recrystallising from alcoholic ether. The product, a brilliant, white powder, consisting of minute, flattened, rhombic crystals, was perfectly free from the odour of valeraldehyde, and melted at 120—121°. It was dried over sulphuric acid and analysed.

I. 0·1935 gram of substance, burnt with copper oxide, gave 30·3 c.c. nitrogen, measured at 16° and 758·4 mm.
II. 0·2890 gram of substance gave 0·2810 gram $BaSO_4$.
III. 0·3171 ,, ,, 0·3138 gram $BaSO_4$.

	Calculated for $CSN_3H_3(C_5H_{10})_2$.	Experiment.			
		I.	II.	III.	
N	18·38 p. c.	18·31	—	—	p. c.
S	13·98 ,,	—	13·36	13·60	,,

The product is, accordingly, a homologue of Nencki's compound; its formation is thus represented:—



$$CSN_2H_4 + 2C_5H_{10}<^{OH}_{NH_2} = CSN_3H_3(C_5H_{10})_2 + NH_3 + 2H_2O.$$

The substance is moderately soluble in cold alcohol, but only very sparingly in ether, which precipitates it from the alcoholic solution. In cold water it is insoluble, but on boiling gradually dissolves with decomposition, evolving valeraldehyde and ammonia. The residual solution, after cooling, gives a black precipitate with ammoniacal silver nitrate. Since the original substance, when dissolved in dilute alcohol, gives with this reagent a curdy, *white* precipitate, the presumption was that thiourea was a product of the decomposition: on applying Claus' test, it was found to be present. The substance breaks down, therefore, under the influence of water, similarly to Nencki's compound:—

$$CSN_3H_3(C_5H_{10})_2 + 2H_2O = CSN_2H_4 + 2C_4H_9{\cdot}CHO + NH_3.$$

Action of Silver Nitrate.—Alcoholic solutions of the constituents were mixed. On the addition of water, the silver derivative separated as a curdy, white precipitate, which was washed, first with much water, then with a little alcohol, and finally with more water. It was free from odour.

When heated in a narrow tube, it begins to darken at about 151°, and appears to melt at 152—153°. A little gas is given off, and the residue instantly changes to a coal-black, solid mass.

A portion was dried over sulphuric acid, and the silver estimated.

0·3749 gram of substance, oxidised by nitric acid, gave 0·1374 gram AgCl.

	Calculated for $C_{11}H_{23}N_3S,AgNO_3$.	Experiment.
Ag	27·03 per cent.	27·04 per cent.

As in the case of the lower homologue, a monomolecular addition compound alone could be obtained. It is much more stable than the corresponding one previously described.

Action of Water upon the Silver Compound.—When boiled with water alone, the (dried) silver compound is very slowly attacked, as it floats, almost unwetted, on the liquid; but on the addition of a little alcohol, which facilitates admixture, decomposition rapidly commences, silver sulphide is produced, and valeraldehyde evolved, whilst thiourea and a nitrate are found in solution.

The decomposition by water may be thus represented:—

$$C_{11}H_{23}N_3S,AgNO_3 + 5H_2O = Ag_2S + CSN_2H_4 + CO(NH_2)_2 \\ 4C_4H_9{\cdot}CHO + 2NH_4{\cdot}NO_3.$$

Action of Acetic Anhydride.—The valeraldehyde compound dissolves readily in hot acetic anhydride; decomposition occurs, and valeraldehyde is freely evolved. The action is thus presumably similar to that with Nencki's compound, but owing to want of material it was not investigated in detail.

Picrate.—Molecular proportions of the valeraldehyde compound and picric acid were mixed in warm alcoholic solution; on cooling, yellow needles separated, and the mixture was exposed freely to the air in order to concentrate further. Next day the needles had given place to a quantity of hexagonal crystals, and the odour of valeraldehyde was distinctly perceptible. The crystals, when recrystallised from water, yielded on analysis 22·15 per cent. of nitrogen; whilst theory would require for the picrate 18·38 per cent. On repeating the experiment, substantially the same phenomena were observed, and the resultant solid contained approximately the same amount of nitrogen as before, namely, 21·80 per cent.

As more or less valeraldehyde was evidently split off, it seemed probable that the picrate had decomposed under the continued standing in contact with alcohol and water; the preparation was therefore again attempted, but on this occasion the yellow needles were filtered off as soon as the solution had become cold, and after being well washed with cold water, were dried over sulphuric acid. This time the odour of valeraldehyde was but faintly noticeable.

A nitrogen determination gave the following result:—

0·2251 gram of substance, burnt with copper oxide, gave 36·5 c.c. measured at 16° and 756 mm., or N = 18·79 per cent.

Calculated for $C_{11}H_{23}N_3S,C_6H_2(NO_2)_3{\cdot}OH$, N = 18·38 per cent.

When heated in a narrow tube, the picrate begins to redden and shrink at 119°; but no further sign of fusion appears below 165°. From this temperature on, the substance gradually softens, but is not completely melted below 192°, when it forms a reddish-black liquid which soon evolves gas.

The nature of the foregoing decomposition was investigated. A preliminary qualitative experiment showed that the substance, when heated in aqueous solution, readily evolves valeraldehyde; whilst a new picrate separates, as the liquid cools, in long, canary-yellow prisms; the latter undergo no change when heated to 200°.

At first the idea suggested itself that this might possibly be the hitherto unknown thiourea picrate,* produced thus:—

$$CSN_3H_3(C_5H_{10})_2,C_6H_2(NO_2)_3{\cdot}OH + 2H_2O = CSN_2H_4,C_6H_2(NO_2)_3{\cdot}OH + 2C_5H_{10}O + NH_3.$$

The crystals, however, proved, on examination, to contain no sulphur; the latter was found in the mother liquor in the form of thiourea. They were purified by recrystallisation from water, dried over sulphuric acid, and completely analysed.

I. 0·2976 gram of substance gave 0·3183 gram CO_2, and 0·0835 gram H_2O, or C = 29·16 per cent.; H = 3·11 per cent.

II. 0·2245 gram of substance gave 44·8 c.c. nitrogen, measured at 18° and 758 mm., or N = 23·12 per cent.

These results indicate that the substance is ammonium picrate.

	Calculated for $C_6H_2(NO_2)_3{\cdot}ONH_4$.	Experiment.
C........	29·24 per cent.	29·16 per cent.
H........	2·44 ,,	3·11 ,,
N........	22·82 ,,	23·12 ,,
O........	45·50 ,,	—

The decomposition occurs as follows:—

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* Thiourea and picric acid do not directly unite (at least under the conditions realised by me) when brought together in either aqueous or alcoholic solution.

$$CSN_3H_3(C_5H_{10})_2,C_6H_2(NO_2)_3{\cdot}OH + 2H_2O = CSN_2H_4 + C_6H_2(NO_2)_3{\cdot}ONH_4 + 2C_5H_{10}O.$$

Urea and Aldehyde-ammonia.

Numerous attempts were made, under various conditions, to cause ordinary urea to interact with acetaldehyde-ammonia, but without success, so far as the production of an oxygen analogue of the thiourea compound is concerned.

Methylthiocarbimide and Aldehyde-ammonia.

Methylthiocarbimide and aldehyde-ammonia, both in warm alcoholic solution, were mixed in the proportions required by the equation

$$CH_3{\cdot}NCS + 2CH_3{\cdot}CH(OH){\cdot}NH_2 = CSN_3H_2(CH_3)(C_2H_4)_2 + 2H_2O.$$

On cooling, the mixture set to a crystalline mass, which was drained on the filter-pump, pressed between folds of bibulous paper, and recrystallised from boiling alcohol. Rosettes of long, snowy-white needles separated, which, after being well washed with cold spirit, and dried over sulphuric acid, amounted to over 70 per cent. of the theoretical.

The formula was checked by a sulphur determination:—

0·3865 gram of substance gave 0·5711 gram $BaSO_4$.

	Calculated for $C_6H_{13}N_3S$.	Experiment.
S	20·13 per cent.	20·32 per cent.

When heated in a narrow tube, the substance melts at 142—143° (uncorr.) to a rich, golden-yellow liquid, which soon changes, with evolution of gas, to a deep mahogany-red.

Boiling alcohol dissolves the compound tolerably freely; but it is somewhat sparingly soluble in the cold. It dissolves readily in cold water, but the aqueous solution, on boiling, at once begins to decompose, ammonia and aldehyde are evolved, and the residual liquid, when concentrated by evaporation, deposits large, well-formed prisms, melting between 117° and 118°. This agrees with the melting point given by Andreasch (*Monats. f. Chem.*, **2**, 277) for methylthiourea, namely, 118°; a sulphur determination established its identity.

I. 0·2909 gram of substance gave 0·7432 gram $BaSO_4$.

	Calculated for $CSN_2H_3(CH_3)$.	Experiment.
S	35·55 per cent.	35·12 per cent.

The decomposition, under the influence of water,* accordingly runs a course similar to that of the thiourea compound; it may be thus formulated:—

$$C_6H_{13}N_3S + 2H_2O = CSN_2H_3{\cdot}CH_3 + 2CH_3{\cdot}CHO + NH_3.$$

On account of this decomposition, the substance is, of course, desulphurised by boiling with alkaline solution of lead.

Picrate.—Like the compounds above described, the methyl derivative also readily unites with picric acid. If warm alcoholic solutions be mixed, golden-yellow, hexagonal plates separate on standing; these are readily soluble in warm water, and, on cooling, come down in beautiful, yellow, iridescent prisms, which can easily, even when working on the small scale, be obtained several inches in length.

After drying over sulphuric acid, the picrate was burnt for nitrogen with the following result:—

0·2027 of substance gave 38·1 c.c. nitrogen, measured at 16° and 759 mm.

	Calculated for $C_6H_{13}N_3S,C_6H_2(NO_2)_3{\cdot}OH$.	Experiment.
N	21·69 per cent.	21·87 per cent.

This salt does not melt at 200°. When heated more strongly, it melts quietly, with decomposition, to a reddish-brown liquid.

A silver nitrate compound could not be obtained pure. On the addition of silver nitrate, and working either in aqueous or alcoholic solution, a sticky, clotted precipitate forms, which is very unstable, beginning to darken almost as soon as produced, and becoming in a few minutes black and tarry. As it was desirable, however, if possible, to investigate the silver nitrate derivatives of the compounds of aldehyde-ammonia with thiocarbimides, in order to compare them with the silver derivatives already described, the action was tried on some other compounds of the class in question.

Action of Silver Nitrate on the Compound of Phenylthiocarbimide with Aldehyde-ammonia.—To 1 mol. proportion of the latter compound,† carefully purified by recrystallisation, and dissolved in strong alcohol cooled by a freezing mixture, 2 mol. proportions of silver nitrate in alcoholic solution were added, also well cooled. A white precipitate was produced which was rapidly filtered off by means of the vacuum-pump, and well washed with ether; neither water nor alcohol is admissible for this purpose, as these liquids both dissolve and decompose the silver compound. The product was dried over sulphuric acid in a vacuum, and the silver estimated.

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* Further investigation with other compounds of this class showed that the behaviour is general; thus the compound of phenylthiocarbimide and aldehyde-ammonia, when boiled with water, gave ammonia, aldehyde, and phenylthiourea; whilst that of benzylthiocarbimide with valeraldehyde-ammonia yielded in like manner benzylthiourea, ammonia, and valeraldehyde. In the latter case, prolonged boiling is necessary to complete the decomposition, as the compound is not only lighter than, and insoluble in, water, but is also wetted by this liquid with some difficulty.

† The constituents of this compound readily unite to form it when fused together in the absence of any solvent.

0·2447 gram of substance, oxidised with nitric acid, yielded 0·1225 gram AgCl.

	Calculated for $C_{11}H_{15}N_3S,2AgNO_3$.	Experiment.
Ag........	38·46 per cent.	38·60 per cent.

As already mentioned, the silver salt is somewhat soluble in water; the solution soon begins to decompose, even at the ordinary temperature, and in a short time becomes black. If warmed with water, the substance blackens immediately; aldehyde is evolved, and silver sulphide deposited as a speculum on the sides of the containing tube. The residual liquid, when cleared by filtration, gives the reaction for a nitrate.

Containing, as it does, 2 mols. of silver nitrate to 1 of base, the silver derivative in question undergoes under the influence of water a change slightly different from those previously described. Thus, when boiled until the smell of aldehyde is no longer perceptible, and filtered from the silver sulphide, the following observations were made:—

1. The liquid is strongly acid to test-paper.

2. Ammoniacal nitrate of silver produces a *white* precipitate, even in the warm solution.

3. No desulphurisation occurs on boiling with alkaline solution of lead.

The latter reactions indicate that the whole of the sulphur has been removed in combination with the silver. Moreover the filtrate is free from silver.

These various facts may be summed up by the equation:—

$$CSN_3H_2(C_3H_5)(C_2H_4)_2,2AgNO_3 + 3H_2O = Ag_2S + 2C_2H_4O + C_6H_5{\cdot}NH{\cdot}CO{\cdot}NH_2 + NH_4{\cdot}NO_3 + HNO_3.$$

A similar derivative was obtained in the case following.

Silver Nitrate and Orthotolylthiocarbimide-aldehyde-ammonia Compound.—Molecular proportions of the orthotolyl compound and silver nitrate were mixed, in cold concentrated alcoholic solution. The liquid darkened somewhat, but scarcely any solid matter separated. On adding excess of the nitrate, a copious, finely-divided precipitate formed, which was quickly filtered off, and well washed with cold, nearly anhydrous, alcohol.

The silver derivative, like the preceding, is very unstable, soon decomposing even in contact with cold alcohol. If water be added to the alcoholic mixture, the solid dissolves, and the solution blackens forthwith.

The substance, when dried over sulphuric acid in a vacuum, gave the following data on analysis:—

0·4148 gram of substance, oxidised with concentrated nitric acid, yielded 0·2055 gram AgCl.

The filtrate from the above yielded 0·1694 gram $BaSO_4$.

	Calculated for $CSN_3H_2(C_7H_7)(C_2H_4)_2,2AgNO_3$.	Experiment.
Ag......	37·52 per cent.	37·29 per cent.
S	5·57 ,,	5·61 ,,

When heated in a narrow tube, the salt darkens at about 85° and by 90° is quite black; if heated quickly on platinum foil, it burns with an explosive puff. On keeping, it gradually darkens, even when quite dry.

The action of water is substantially the same as in the case of the corresponding phenyl compound. The solid is decomposed, gradually by cold water, or at once on warming; aldehyde is evolved, and the tube brilliantly coated with a mirror of silver sulphide. The filtrate gives the reaction for nitric acid, and is strongly acid to test-paper. It gives no perceptible black coloration with ammoniacal silver nitrate, but is nevertheless not absolutely free from sulphur; for, on boiling with alkaline lead solution, a trifling desulphurisation occurs. Further examination showed the reason of this; the substance on treatment with water—even on washing—loses a trace of silver, which passes into solution, and can be detected in the filtrate by the addition of dilute hydrochloric acid. The substance having thus become somewhat poorer in silver, is not perfectly desulphurised on boiling with water. The action may be substantially represented as follows:—

$$CSN_3H_2(C_7H_7)(C_2H_4)_2,2AgNO_3 + 3H_2O = Ag_2S + C_7H_7{\cdot}NH{\cdot}CO{\cdot}NH_2 + 2C_2H_4O + NH_4{\cdot}NO_3 + HNO_3.$$

Thus it appears that the silver nitrate derivatives of the thiocarbimide compounds selected as representatives of their class agree in composition and in the mode of their interaction with water.

Action of Acetic Anhydride on the Orthotolylthiocarbimide-aldehyde-ammonia Compound.—A quantity of this substance, purified by repeated recrystallisation,* was added, little by little, to excess of acetic anhydride, the latter being warmed on the water-bath; aldehyde was freely evolved, and the solid dissolved, forming a deep-red solution. When the odour of aldehyde ceased to be perceptible, the mixture was thrown into water; a brown, curdy mass separated, which, on washing with alcohol, became white. After two recrystallisations from boiling alcohol (in which it is only moderately soluble), the substance was obtained in beautiful, white, glittering prisms, insoluble in water, and melting at 184° (uncorr.). From its appearance, melting point, &c., it was evidently identical with the acetylorthotolylthiourea which I previously described (Trans., 1889, 304) as prepared from acetylthiocarbimide and orthotoluidine.

A sulphur estimation gave the following result:—

0·2017 gram of substance gave 0·2402 gram $BaSO_4$.

	Calculated for $CSN_2H_2(C_7H_7)\cdot CO\cdot CH_3$.	Experiment.
S	16·68 per cent.	16·37 per cent.

The product is accordingly acetylorthotolylthiourea, and the interaction runs the same course as in the case of the corresponding phenyl compound. It may be noted that the melting point of the ortho- is higher than that of the para-tolylthiourea; the latter, according to Miquel (*Bull. Soc. Chim.*, **28**, 103), melts at 175—176°.

Phenylcarbimide and Aldehyde-ammonia.

If a mixture of these substances be gently warmed on the water-bath, a violent action occurs, the isocyanate disappears, and a brittle, white solid is formed, from which the new compound can be easily isolated. It was found better, however, to operate as follows:—

Aldehyde-ammonia, dissolved in as little absolute alcohol as possible, was well diluted with anhydrous ether, and added to an equal weight of phenylcarbimide, also freely diluted with ether. Most of the latter was distilled off on the water-bath, and the solid residue (which was quite free from the odour of isocyanate) collected and purified by recrystallisation from much boiling alcohol. The substance was thus obtained as a felted mass of very delicate, white needles, having a beautiful satiny lustre, and melting, with decomposition, at 199—200° (uncorr.) to a mahogany-red liquid.

It is insoluble in water and in benzene; very sparingly soluble in boiling alcohol or carbon bisulphide, almost insoluble in the cold.

It was dried at 100° and analysed, with the following results:—

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* If this purification be omitted, the product is a black, tarry oil, from which scarcely any solid matter can be extracted.

I. 0·2222 gram of substance gave 0·5229 gram CO_2 and 0·1458 gram H_2O.

II. 0·2312 gram of substance gave 40·7 c.c. nitrogen, measured at 19° and 755 mm.

These figures lead to the formula $C_{11}H_{15}N_3O$.

	Theory.	Experiment.
C	64·30 per cent.	64·18 per cent.
H	7·32 ,,	7·30 ,,
N	20·53 ,,	20·23 ,,
O	7·85 ,,	—

This substance is therefore the oxygen analogue of that resulting from the interaction of phenylthiocarbamide with aldehyde-ammonia; its formation occurs thus:—

$$C_6H_5\cdot NCO + 2CH_3\cdot CH(OH)\cdot NH_2 = C_{11}H_{15}N_3O + 2H_2O.$$

It is more stable than the corresponding sulphur compound; when boiled with water alone, it is not sensibly attacked, but on the addition of dilute hydrochloric acid it dissolves readily, and with evolution of aldehyde. From the residual liquid, on cooling, colourless needles separate, sparingly soluble in cold water, melting at 143—144°, and further characterised as carbanilamide by the following reactions:—

1. When heated in a dry tube, ammonia is evolved, and a crystalline sublimate forms.

2. The latter, on further heating, emits the pungent odour of phenylcarbimide.

$$2C_6H_5\cdot NH\cdot CO\cdot NH_2 = CO(NH_2)_2 + CO(NH\cdot C_6H_5)_2.$$
$$3CO(NH_2)_2 = H_3C_3N_3O_3 + 3NH_3.$$
$$CO(NH\cdot C_6H_5)_2 = C_6H_5\cdot NCO + C_6H_5\cdot NH_2.$$

Thus, in its decomposition by (acidified) water, this substance behaves like its sulphur analogue:—

$$CON_3H_2(C_6H_5)(C_2H_4)_2 + 2H_2O = C_6H_5\cdot NH\cdot CO\cdot NH_2 + 2C_2H_4O + NH_3.$$

A number of experiments was made with the view of acquiring some further information regarding the chemistry of the thiocarbimide derivatives; a few of these may be mentioned.

1. *Action of Nascent Hydrogen upon the Phenyl Compound.*—This experiment was undertaken in order to ascertain whether the two aldehyde groups would be split off along with one of the nitrogen atoms, so as to yield diethylamine, thus:—

$$C_6H_5\cdot CSN_3H_2(C_2H_4)_2 + 4H = CSN_2H_3\cdot C_6H_5 + NH(C_2H_5)_2.$$

Owing to the instability of the compound, neither strongly acid nor alkaline reducing media could be employed; it was therefore treated with sodium amalgam, dilute hydrochloric acid being added from time to time, so as to keep the mixture faintly acid. Under these conditions, decomposition took place, but not in the sense hoped for; the escaping hydrogen smelt of aldehyde, and in the residue were found sodium and ammonium chlorides, together with a substance melting at 150°, and easily recognised as monophenylthiourea:—

$$C_{11}H_{15}N_3S + 2H_2O = CSN_2H_3{\cdot}C_6H_5 + 2CH_3{\cdot}CHO + NH_3.$$

2. *Desulphurisation of the Phenyl Compound.*—Two experiments were made in this direction:—

In the first, the compound was desulphurised by freshly-precipitated yellow oxide of mercury, in presence of aniline. As before, the molecule broke down, with evolution of aldehyde; the desulphurisation product was a deep brownish-red, tenacious, basic oil.

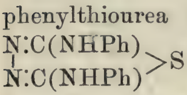
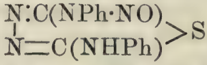
In the second, the substance was treated alone, the conditions being otherwise the same as when aniline was present. A solid was thus obtained, which, on recrystallisation, came down in woolly masses of fine needles. These melted at 199—200°, were freely soluble in alcohol and hot water, sparingly in the cold, and, on heating with dilute hydrochloric acid, *evolved no aldehyde.* The amount of material obtained was too small to admit of a complete examination, but I did not consider it necessary to pursue this subject further, my immediate object being merely to ascertain whether the phenyl compound would yield, on desulphurisation, a substance identical with the phenyl isocyanate-aldehyde-ammonia product. That this was not the case followed as well from the negative result on hydrochloric acid treatment, as from the ready solubility of the compound in alcohol and hot water.

3. *Action of Nitrous Acid on the Phenyl Compound.*—A quantity of the latter substance was mixed with alcohol, a slight excess of dilute hydrochloric acid added, and then, little by little, a concentrated aqueous solution containing excess of sodium nitrite. At first the mixture cleared and assumed a green colour, but as the addition of the nitrite was continued, it began to become turbid; and, after a short time, a lemon-yellow, crystalline solid separated, which, in the crude state, smelt of phenylthiocarbimide. This, when collected, washed well with spirit, and recrystallised from much boiling alcohol, was obtained in delicate, canary-yellow, odourless needles, which at 183—184° (uncorr.) decomposed with an explosive puff. When dissolved in phenol and treated with a few drops of sulphuric acid, a deep purple-red coloration is produced, which, on the addition of water and excess of caustic alkali, changes to a beautiful, azure-blue (Liebermann's nitroso-reaction).

Though a nitroso-substance, it is *not* a derivative of the aldehyde-ammonia compound; here, as in many other cases, decomposition occurs, and the product is a derivative of the resultant monophenylthiourea.

This compound does not volatilise in a current of steam; is practically insoluble in water, ether, chloroform, benzene, and hydrochloric acid, very sparingly in boiling alcohol, still less so in the cold; slightly in boiling glacial acetic acid, by which, however, it is to some extent decomposed. Cold, concentrated sulphuric acid readily dissolves the substance, producing a beautiful scarlet liquid, which changes to purple on warming. It is insoluble in cold aqueous potassium hydroxide, but dissolves easily in alcoholic, giving a bright, scarlet solution resembling the preceding; this liquid is decolorised by warming alone, or desulphurised by heating with alkaline solution of lead.

On treating phenylthiourea with nitrous acid in like manner, a yellow solid was obtained, which, in the crude state, smelt faintly of phenylthiocarbimide. By recrystallisation from much boiling alcohol, delicate, canary-yellow needles were obtained; these deflagrated at 184°, gave Liebermann's reaction, yielded with sulphuric acid the scarlet and purple colorations, and, in short, were identical with the nitroso-compound previously described.

Nitrous acid, according to Hector (*Ber.*, **22**, 1177), acts upon phenylthiourea to form a basic substance dianilido-oiazothiole,  $\left.\begin{array}{l}\mathrm{N{:}C(NHPh)}\\ \mathrm{N{:}C(NHPh)}\end{array}\right>\mathrm{S}$. No details are given regarding its preparation from these materials, but from a description of its properties, it was evidently different from the compound in question. Amongst its derivatives, however, a substance is briefly referred to as nitrosodianilido-oiazothiole,  $\left.\begin{array}{l}\mathrm{N{:}C(NPh{\cdot}NO)}\\ \mathrm{N{=}C(NHPh)}\end{array}\right>\mathrm{S}$, obtained by the action of nitrous acid on the base. This is described as a yellow powder, insoluble in water and alcohol; it puffs at 179°. There could be little doubt that the substance which I obtained by the direct action of excess of nitrous acid on the aldehyde-ammonia compound, and on phenylthiourea, was Hector's nitroso-compound, but in a pure condition. A nitrogen determination (made with the aldehyde-ammonia product) showed this to be the case:—

0·1635 gram of substance gave 34 c.c. nitrogen, measured at 20° and 748 mm.

	Calculated for $C_{14}H_{11}N_5SO$.	Experiment.
N	23·62 per cent.	23·57 per cent.

From orthotolylthiourea,* by similar treatment, a corresponding nitroso-derivative was obtained, together with a yellow, sticky, semi-solid material. The former (not recrystallised) occurs in long, yellow needles, insoluble in water, moderately soluble in alcohol, and melting, with copious effervescence, at 150—151°, to a mahogany-brown liquid. It gives Liebermann's reaction, and yields with cold alcoholic potash a bright, scarlet solution, but dissolves in sulphuric acid without colour-change.

Ethylthiourea and Nitrous Acid.

Interaction occurred with much effervescence, a disgusting iso-cyanide-like odour was produced, and soon drops of a yellow oil separated. The latter, when extracted with ether, and the ether distilled off, was miscible with alcohol, freely desulphurised on treatment with alkaline lead solution, gave no colour with alcoholic potash, and smelt pungently of ethylthiocarbimide. The equation representing the production of this substance may be written thus:—

$$CSN_2H_3{\cdot}C_2H_5 + HNO_2 = C_2H_5{\cdot}NCS + N_2 + 2H_2O\ ;$$

but it by no means expresses the whole action, for amongst the products sulphuric acid was identified, recognised both by barium nitrate and by its charring effect on paper.

In another experiment where a considerable excess of nitrite was employed, no ethylthiocarbimide was detected, but the resultant solution contained much free sulphuric acid.

Allylthiourea was treated in like manner with a similar result; the mixture smelt, first of isocyanide, then pungently of mustard oil, and sulphuric acid was found in the solution.†

Thiourea and Nitrous Acid.

Earlier in the present paper (p. 512), Claus' test for thiourea is mentioned. According to this chemist (see also *Ber.*, **4**, 140; and **6**, 726), the production of a blood-red coloration with ferric chloride, after previous treatment of thiourea with ethyl nitrite, is due to the conversion of the urea into the metameric ammonium thiocyanate. No explanation is offered regarding the mechanism of the production of the latter substance, which, moreover, was not isolated; and, indeed, no further experimental evidence of its presence is adduced than the ferric chloride reaction, and the fact that a yellow substance was obtained resembling in the main pseudosulphocyanogen (though the analytical data diverged considerably from those required by theory), which yellow substance resulted also on treatment of ammonium thiocyanate with nitrous acid under similar conditions.

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* The melting point given by Staats (*Ber.*, **13**, 136) for this compound, namely, 155°, is somewhat low; a preparation made from orthotolylthiocarbimide and ammonia, and purified by recrystallisation from water, melted at 160—161° (uncorr.). A specimen of pure di-orthotolylthiourea was found to melt at 159° (uncorr.); the melting points recorded by Girard (*Ber.*, **4**, 985) and Berger (*ibid.*, **12**, 1854) are 165° and 156° respectively.

† This action appears to be very complicated. Not only were the above phenomena observed, and some evidence of the presence of Hector's diallyldithiotetrahydrotriazole (Abstr., 1892, 292) obtained, but also of at least one other product, to which he does not appear to refer. At present, I have not access to his original paper.

But as more or less thiocarbimide was produced by the action of this acid upon the monosubstituted thioureas above mentioned, it seemed worth while to try whether thiourea really underwent conversion into an ammonium compound. For if the action proceeded upon the same lines as where the substitution derivatives are concerned, free thiocyanic acid, rather than ammonium thiocyanate, might be expected.

An experimental investigation of the action was therefore commenced, the detailed study of which, as well as that of nitrous acid upon the substituted thioureas generally, was interrupted when I learned that Hector desired to reserve it. But the following qualitative data, which bear chiefly on the first stage of the decomposition, may be here recorded.

On mixing a solution of thiourea* in dilute spirit with ethyl nitrite, the mixture became first deep red, then yellow, and a gas containing free nitrogen and its oxides was evolved with effervescence. A portion of the resultant clear solution was freely diluted with water and divided into two parts; to one of these, ferric chloride was added, and to the other, Nessler's reagent. In the former, the rich blood-red thiocyanate coloration appeared; whilst the latter gave no indication of the presence of ammonia, but a pale, primrose-yellow, finely-divided precipitate formed. For the purpose of comparison, a solution of ammonium thiocyanate was prepared, giving with ferric chloride a colour of the same depth as that previously obtained; a portion of this solution, when treated with Nessler's reagent, gave the deep, orange-brown coloration and turbidity characteristic of ammonium salts.

The remainder of the former solution contained in a dish was placed in a desiccator over oil of vitriol, the dish being surrounded by pieces of filter-paper moistened with solution of ferric chloride. The air was exhausted, and in a short time the pieces of paper became intense blood-red, indicating the presence of the volatile thiocyanic acid. As the liquid concentrated, a quantity of a flocculent canary-yellow material separated; this, when filtered off and washed thoroughly with water,* dissolved in hot alkali; but the solution, after continued boiling and subsequent acidification with acetic acid, gave with lead acetate no yellow precipitate; and another portion, similarly boiled with alkali, and then treated with excess of hydrochloric acid, gave with ferric chloride no red coloration: from which it may be concluded that the yellow reaction product does not consist of pseudosulphocyanogen.

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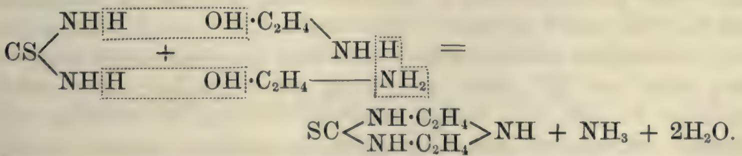
* Similar results were obtained when (as in Claus' experiments) the solid substance was employed.

According to Storch (Abstr., 1891, 548), nitrous acid (amongst other oxidising substances) converts thiourea in acid solution into the bisulphide, $NH{:}C(NH_2){\cdot}S{\cdot}S{\cdot}(NH_2)C{:}NH$; but the substance in question does not seem to be identical with this bisulphide. The ultimate decomposition is evidently profound, for a portion of the sulphur was found in the form of free sulphuric acid. But in part, at least, it appears to be expressible thus:—

$$CSN_2H_4 + HNO_2 = HSCN + N_2 + 2H_2O.$$

Substituted Thioureas and Aldehyde-ammonia.

In the communication to which reference has already been made, a suggestion was thrown out regarding the mechanism of the thiocarbimide-aldehyde-ammonia interaction, which would bring it into line with the thiourea process. This was to the effect that, a molecule of ammonia splitting off from two of aldehyde-ammonia, the former might unite with the thiocarbimide to form a substituted thiourea, which in turn combines with the aldehyde-ammonia residue to form the new compound. With thiourea itself, the action would run a similar course, save that the molecule of ammonia split off would be liberated. By combining the mono-substituted thioureas, therefore, with aldehyde-ammonia, the same products should be obtained as those afforded by the corresponding thiocarbimides; whilst from di-substitution derivatives, compounds should in like manner be formed containing two alkyl groups. Thus, using the provisional formulæ before employed—



$$\mathrm{CS}\left\langle\begin{matrix}\mathrm{NH}\,\boxed{\mathrm{H\qquad OH}}\cdot\mathrm{C_2H_4}\diagdown \\ \qquad + \qquad\qquad \mathrm{NH}\,\boxed{\mathrm{H}} \\ \mathrm{NH}\,\boxed{\mathrm{H\qquad OH}}\cdot\mathrm{C_2H_4}\text{——}\boxed{\mathrm{NH_2}}\end{matrix}\right. = \mathrm{SC}<\begin{matrix}\mathrm{NH\cdot C_2H_4}\\ \mathrm{NH\cdot C_2H_4}\end{matrix}>\mathrm{NH} + \mathrm{NH_3} + 2\mathrm{H_2O}.$$

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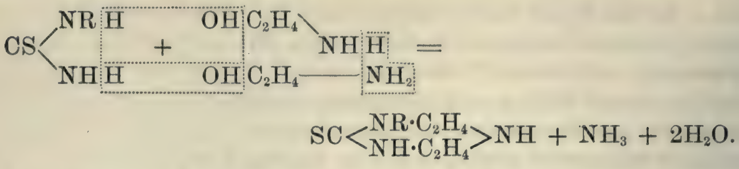
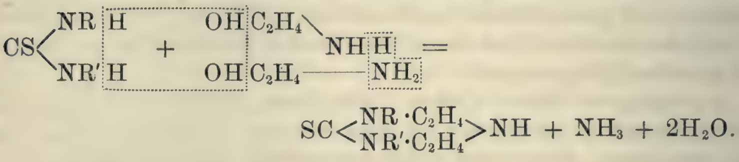
* The filtrate was still found to be free from ammonium salts, though giving an intense thiocyanic acid reaction. It should be added that only a small portion of the latter appears to be in the free state.



$$=\ SC{<}\begin{smallmatrix}NR\cdot C_2H_4\\ NH\cdot C_2H_4\end{smallmatrix}{>}NH + NH_3 + 2H_2O.$$



$$=\ SC{<}\begin{smallmatrix}NR\cdot C_2H_4\\ NR'\cdot C_2H_4\end{smallmatrix}{>}NH + NH_3 + 2H_2O.$$

In attempting to realise these latter interactions, the following compounds were used, together with acetaldehyde-ammonia :—

$CSN_2H_3\cdot CO\cdot CH_3$.
$CSN_2H_3\cdot C_3H_5$.
$CSN_2H_3\cdot C_6H_5$.
$CSN_2H_2(C_3H_5)\cdot C_6H_5$.
$CSN_2H_2(C_6H_5)_2$.

Numerous experiments were made, the conditions being varied as regards (1) the nature of the solvent employed; (2) the degree of concentration of the solutions; (3) the time (this was varied from a few minutes to months); (4) the temperature; and (5) the presence or absence of acid. Under none of the conditions attained was the desired combination effected.

It now remains to describe some instances in which the interaction between certain thiocarbimides and aldehyde-ammonias proceeds upon lines differing from those hitherto recorded.

Phenylthiocarbimide and Chloral-ammonia.

These, in the proportions of 1 mol. of the former to 2 of the latter, were mixed in concentrated alcoholic solution, and the mixture warmed to just below its boiling point. The now somewhat red liquid was decanted from a trace of white, amorphous precipitate, and the clear liquid set aside. On standing for a short time, colourless, well-formed prisms began to separate; these contained no chlorine; melted at 153°; were moderately soluble in hot water, nearly insoluble in cold, and tasted extremely bitter; on warming with alkaline solution of lead, they gave the galena reaction readily. Analysis was unnecessary, as the substance was obviously phenylthiourea. Therefore the expected chlorinated derivative,

$$CSN_3H_2(C_6H_5)(CH\cdot CCl_3)_2,$$

is not the product of this action; but the elements of NH_3, having been removed from the chloral-ammonia, combine with the thiocarbimide to form phenylthiourea.

It was thought that the heating to which the mixture had been subjected might possibly have facilitated the decomposition of the chloral-ammonia into its constituents; but on employing cold solutions interaction took place, with precisely similar results.

This rather unexpected behaviour of chloral-ammonia with phenylthiocarbimide led to an experiment to ascertain whether the former would combine with thiourea to yield a chlorinated derivative of Nencki's acetaldehyde compound.

Theoretical quantities of the constituents were heated together in alcoholic solution, whereby some decomposition occurred, and the mixture became reddish, but, on evaporating the solvent, the residue was found to be thiourea. It is worthy of remark that the latter separated in large, thin, six-sided plates; on recrystallisation from water, these were obtained in the ordinary rhombic form.

Some experiments were carried out with thiocarbimides containing acid radicles; these (sometimes termed thiocyanates) are obtained by the action of the corresponding acid chloride upon lead thiocyanate (Miguel, *Ann. Chim. Phys.* [5], **11**, 295). In this connection, it is interesting to note that the acetyl compound was evidently originally obtained by Nencki, who records (*Ber.*, **6**, 599) that "on heating acetylthiourea with phosphoric anhydride, a pungently-smelling oil distilled over, which sank in water." The considerable carbonisation which occurred, and consequent small yield, prevented his further examining the product. But the latter was doubtless identical with the so-called "acetyl thiocyanate," which, four years later, Miguel (*loc. cit.*) obtained as an excessively pungent smelling liquid, of sp. gr. 1·151.

Acetylthiocarbimide reacts with extreme readiness. The following observations were made in a case where alcohol had been employed to dilute the liquid.

15 grams of acetylthiocarbimide were added to about the same bulk of cold, nearly anhydrous alcohol. After the lapse of some minutes, a violent action took place, by which a considerable portion of the contents was projected out of the containing tube. Ethyl acetate was readily recognised, by its odour, as one of the products:—

$$CH_3{\cdot}CONCS + C_2H_5{\cdot}OH = CH_3{\cdot}COOC_2H_5 + HSCN,$$

but the decomposition had gone far beyond this; on pouring away the remaining liquid, which still smelt pungently of the thiocarbimide, yellow pellets were found, varying in size from duck shot downwards. These were hard and brittle, burned with a blue flame, evolving sulphurous anhydride, and consisted of fused sulphur. The principal residue was a deep-yellow powder, insoluble in water, but soluble in concentrated sulphuric acid and in caustic alkalis; the latter solution, when boiled for some time and subsequently acidified with hydrochloric acid, gave a blood-red coloration with ferric chloride. Further, the soda solution, when boiled and treated with excess of acetic acid, gave a yellow precipitate with lead acetate. These reactions, as well as the appearance of the substance, characterised it as pseudosulphocyanogen.

Acetylthiocarbimide and Aldehyde-ammonia.

These substances interact readily with evolution of much heat, but, unless careful attention be paid to conditions, the process tends to become complicated, and sticky or tarry matters are produced. After many trials, using different methods, the following was found to give the most satisfactory result.

12·2 grams of aldehyde-ammonia were dissolved in the least possible quantity of almost anhydrous alcohol, the solution largely diluted with anhydrous ether, and well cooled by a freezing mixture. To this was added, little by little, a solution of 20·2 grams of pure and freshly-distilled acetylthiocarbimide in about 2½ times its volume of anhydrous ether, the latter solution being also strongly cooled. The mixture, greenish at first, became yellow during the addition of the second half of the thiocarbimide solution, and a slight precipitate gradually formed.

The product was now exposed freely to the air in an open dish; as the solvent evaporated, a white solid separated, which was removed by filtration, and the mother liquor set aside. This process was continued, and successive crops of solid substance collected, until the filtrates, now red in colour, began to become syrupy. The mixed residues were washed with ether and twice recrystallised from alcohol, then treated with a small quantity of hot water, and the mixture filtered. On cooling, this filtrate first deposited a trifling quantity of short, well-formed prisms, and then almost solidified from separation of woolly-looking masses of fine, slender needles; the former adhered to the surface of the containing vessel, so that the remaining crystals could be readily separated, by inverting the dish and allowing its free contents to fall out. The latter were well washed with cold water. and dried over sulphuric acid in a vacuum.

On analysis, the following data were obtained:—

0·2032 gram of substance gave 0·3043 gram CO_2 and 0·1375 gram H_2O.

0·2033 gram of substance gave 36·6 c.c. nitrogen, measured at 16° and 757·5 mm.

0·2072 gram of substance gave 36·8 c.c. nitrogen, measured at 17° and 763 mm.

0·1994 gram of substance gave 0·2305 gram $BaSO_4$.

From which results the formula $C_7H_{15}N_3SO_2$ is deduced.

	Calculated.	Experiment.	
C........	40·93 per cent.	40·83 per cent.	
H........	7·32 ,,	7·58 ,,	
N........	20·53 ,,	20·91 ,,	20·68
S........	15·62 ,,	15·89 ,,	
O........	15·60 ,,	—	

The interaction may be thus represented :—

$$2CH_3{\cdot}CH(OH){\cdot}NH_2 + CH_3{\cdot}CO{\cdot}NCS = C_7H_{15}N_3SO_2 + H_2O.$$

On comparing this with the equation representing the action between acetaldehyde-ammonia and the thiocarbamides containing hydrocarbon radicles, it is noticeable that, whilst in both cases union occurs in the proportion of 1 mol. of thiocarbamide to 2 mols. of aldehyde-ammonia, in the present instance only a single molecule of water is eliminated. The idea that the interaction might have run the ordinary course, but that the product was a hydrate, was negatived, for a quantity of the substance, dried in the cold over sulphuric acid, underwent no perceptible alteration in weight after being heated for an hour at 100°. This acetyl derivative, therefore, holds in distinct chemical combination the elements of a molecule of water more than its congeners.

The substance gives no colour-reaction on the addition of ferric chloride. With ammoniacal silver nitrate, a yellow coloration is produced, which rapidly gives place to a copious black precipitate; and the sulphur is also very readily removed by warming with alkaline solution of lead. It is scarcely attacked by boiling water alone, but is at once decomposed on heating with dilute hydrochloric acid, with evolution of aldehyde.

It is readily soluble in boiling water, sparingly in cold; very freely in hot alcohol, moderately in cold; slightly soluble in hot benzene, practically insoluble in ether. When purified by repeated crystallisation from aqueous alcohol, the substance melts at 187° (uncorr.) with effervescence to a brown liquid, which rapidly acquires a deep bromine-red colour. The melting point is, however, extremely sensitive to impurities, and traces of the latter, which chemical analysis fails to detect, will lower it by nearly 10°.

Benzoylthiocarbimide and Aldehyde-ammonia.

Since the former substance, according to Miguel, is a true thiocarbimide, it was anticipated that the interaction between these would run a course parallel to that of the alkylthiocarbimides. Experiment has failed to verify this expectation.

The two constituents were mixed in concentrated alcoholic solution, with cooling by water. In about an hour crystals began to form in the brownish liquid, and after 12 hours the separation was complete; the solid product was drained on the filter pump, washed with spirit, and recrystallised twice from alcohol. As thus obtained, the substance forms vitreous, oblique prisms, perfectly colourless, and melting at 170—171° (uncorr.).

On the addition of ammoniacal silver nitrate to the alcoholic solution, a black precipitate falls; and on treatment with alkaline lead solution, a very brilliant galena speculum is produced. But on boiling with dilute hydrochloric acid not a trace of aldehyde was evolved; it was, therefore, improbable that the compound

$$CSN_3H_2(CO{\cdot}C_6H_5)(C_2H_4)_2$$

was in hand; this suspicion was confirmed by the results of analysis.

0·2302 gram of substance gave 30·2 c.c. nitrogen, measured at 11° and 749 mm.

0·2275 gram of substance gave 0·2974 gram $BaSO_4$.

These data lead to the conclusion that the substance is benzoylthiourea.

	Calculated for $CSN_2H_3{\cdot}CO{\cdot}C_6H_5$.	Experiment.
N	15·59 per cent.	15·37 per cent.
S	17·79 ,,	17·97 ,,

The melting point of this compound is given by Pike (*Ber.*, **6**, 755) as 169—170°; and by Miguel (*Ann. Chim. phys.* [5], **11**, 313) as 171°; as already stated, the melting point observed lies between 170° and 171°. The substance, moreover, is sparingly soluble in cold water, and has an extremely bitter taste.

In the interaction, therefore, between benzoylthiocarbimide and aldehyde-ammonia, only the elements of NH_3 in the latter compound have taken part—

$$C_6H_5{\cdot}CO{\cdot}NCS + NH_3 = CSN_2H_3{\cdot}CO{\cdot}C_6H_5.$$

The experiment was several times repeated, and the conditions varied, but without affecting the result.

It may here be added, that benzoylthiourea dissolves in benzene and in chloroform, crystallising from either in brilliant, silvery prisms. It is soluble also, without decomposition, in concentrated sulphuric acid, from which it separates on dilution with water in fine, silvery needles.

The information now acquired regarding the acetaldehyde- and valeraldehyde-ammonia compounds of thiourea on the one hand, and the alkylthiocarbimide derivatives of aldehyde-ammonia, may be generally stated as follows:—

a. They combine with picric acid, forming equimolecular additive compounds.

b. They are decomposed by hot acetic anhydride, with elimination of both aldehyde groups, together with one of the three nitrogen atoms, and production of the corresponding acetylated thiourea.

c. Boiling with water effects an analogous decomposition, save that the resultant thiourea is not acetylated.

d. They combine with silver nitrate, yielding sparingly soluble additive products, which are more or less unstable in presence of water.

From the striking resemblance in the behaviour of these compounds, the conclusion may, I think, be fairly drawn that they are all members of the same class. Their decompositions, so far as they have been studied, all proceed upon the same lines, and the only point of distinction observed between the thiocarbimide and the thiourea compounds lies in the power which the molecules of the former possess, of uniting with 2 mols. of silver nitrate, whilst those of the latter, under the same conditions, can hold but one. But even amongst these metallic derivatives, the resemblance otherwise still holds; all readily break down on mere contact with hot water, and the resultant decompositions run essentially the same course. In each case, the two aldehyde groups, as such, are split off, and one-third of the nitrogen leaves the compound in the form of ammonia; the residual nitrogen is found either as a urea or a urea *plus* a thiourea, according to the amount of metal present. From the nature and uniformity of these changes, it may be inferred: first, that the two aldehyde groups, existing as such, together with a nitrogen atom, occupy a constant position in the molecule; and, secondly, that the remainder of the molecule is a thiourea residue.

What the structure of the former portion may be is still rather obscure; for, though the uniformity in decomposition is highly suggestive of similarity in structure, it does not throw much light upon the atomic arrangement.

But whilst the constitution of this aldehydic fraction of the molecule still requires further examination, the present investigation has brought to light some interesting observations bearing upon that of the residual portion, which observations tend to corroborate the conclusions drawn by Professor Emerson Reynolds (Trans., 1891, 394) from an experimental study of the thiocarbamidammonium compounds.

In the communication in question, it is pointed out that, whilst thiourea readily unites with ammonium chloride, bromide, and iodide, and (though less readily) with di-, tri-, and tetr-ethyl ammonium bromides, on the other hand, none of these compounds could be caused to combine with substituted thioureas. Adopting the view that union occurs by means of the nitrogen, the author reasons that "the loss of power of combination with ammonium bromide when but one atom of hydrogen in thiocarbamide is displaced by a more positive radicle, such as ethyl or phenyl, is inconsistent with the symmetrical constitution of thiocarbamide, which should still have an NH_2 group unaffected and available for union, but is quite consistent with its unsymmetrical structure." On this and other grounds he considers that the constitution is best expressed by the unsymmetrical formula $HN{:}C{<}^{NH_2}_{SH}$. In the case of monosubstitution derivatives the choice lies between $RN{:}C{<}^{NH_2}_{SH}$ and $HN{:}C{<}^{NHR}_{SH}$, preference being given to the former, as according best with the genesis of these compounds from RNCS and ammonia; and he explains the failure of the monosubstituted thioureas to yield addition products with ammonium haloïds, by suggesting that "the presence of the positive radicle in the imidic group paralyses the power of combination, which appears in consequence to be exclusively due to the NH of the substance we have been accustomed to term thiocarbamide."

The results obtained on treating aldehyde-ammonia with thiourea and its substitution derivatives respectively, not only afford evidence of the unsymmetrical nature of these molecules, but also, I think, support the view above quoted. For the fact that thiourea interacts quite as readily with valeraldehyde-ammonia as with its lower homologue indicates that combination is not specially dependent upon the nature of the aldehydic hydrocarbon residue. But, in sharp contrast to this, is the fact that even a single substitution in the thiourea suffices to completely destroy its power of interaction; just as in the cases cited by Professor Reynolds, it paralysed its power of forming addition compounds.

Whilst admitting the unsymmetrical structure of the mono-substitution derivatives,* it might, however, be argued that their generation from RNCS and ammonia, though evidence in favour of the formula $\mathrm{RN{:}C}<^{\mathrm{NH_2}}_{\mathrm{SH}}$ does not necessarily exclude the other—$\mathrm{HN{:}C}<^{\mathrm{NHR}}_{\mathrm{SH}}$; that power of interaction or combination may be determined by the NH_2, but lost when this becomes NHR.

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* Moreover, evidence gained from a study of the melting points of these com-

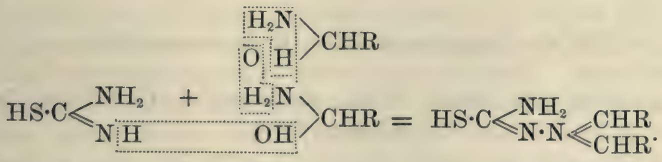
It was hoped that a study of the action of nitrous acid on these compounds might serve to decide between the above formulæ. For, assuming the structure to be $\mathrm{NH{:}C}<^{\mathrm{NHR}}_{\mathrm{SH}}$, a nitroso-compound might be expected to result; but this, as already shown, is not the case. On the other hand, if the substances in question are of the form $\mathrm{RN{:}C}<^{\mathrm{NH_2}}_{\mathrm{SH}}$, the non-formation of a nitroso-derivative is intelligible; here the attack on the amidic group might give rise to an unstable alkylimidothiocarbonic acid, $\mathrm{RN{:}C}<^{\mathrm{OH}}_{\mathrm{SH}}$, which, by loss of the elements of water, could yield the corresponding thiocarbimide—a compound which (though in small proportion) is actually formed. And in like manner the formation of thiocyanic acid from thiourea is explicable :—

$$(1.)\ \mathrm{NH{:}C}<^{\mathrm{NH_2}}_{\mathrm{SH}} + \mathrm{HNO_2} = \mathrm{NH{:}C}<^{\mathrm{OH}}_{\mathrm{SH}} + \mathrm{N_2} + \mathrm{H_2O}.$$

$$(2.)\ \mathrm{NH{:}C}<^{\mathrm{OH}}_{\mathrm{SH}} = \mathrm{H_2O} + \mathrm{HSCN}.$$

But the action of nitrous acid, under the conditions stated, is unfortunately for this purpose, far from simple; and hence scarcely allows of any definite conclusion being drawn.

The bearing of the foregoing upon the constitution of Nencki's compound and its homologue, and the thiocarbimide derivatives of aldehyde-ammonias, remains to be considered. Assuming that, in the former, interaction occurs exclusively through the imidic group, their production may be thus represented :—



$$\mathrm{HS{\cdot}C}<^{\mathrm{NH_2}}_{\mathrm{NH}} + {}^{\mathrm{H_2N}}_{\mathrm{OH}}{>}\mathrm{CHR} + {}^{\mathrm{H_2N}}_{\mathrm{OH}}{>}\mathrm{CHR} = \mathrm{HS{\cdot}C}<^{\mathrm{NH_2}}_{\mathrm{N{\cdot}N}<^{\mathrm{CHR}}_{\mathrm{CHR}}}.$$

pounds points to the conclusion that they differ in structure from the disubstituted thiocarbamides. But as there is considerable reason for believing the latter to be symmetrical—at least in the solid state—it may be inferred that the former are not. I hope later on to make a communication on this subject.

But the close resemblance in general properties and decompositions between these and the thiocarbimide compounds affords, as already pointed out, strong evidence of similarity in structure; in which case the latter would have to be regarded as substitution derivatives of the form, $HS\cdot C\lessdot\begin{array}{l}NHR'\\N{-}N\lessdot\begin{array}{l}CHR\\CHR\end{array}\end{array}$.

Such a derivative, however, in breaking down so as to afford the corresponding substituted thiourea must either yield an isomeric compound of the form $HS\cdot C\lessdot\begin{array}{l}NHR'\\NH\end{array}$, or the radicle must alter its position. There is no substantial ground for the latter assumption, but the observed phenomena may, I think, be explained as follows:—In the case of thiourea, both amidic and imidic groups simultaneously giving up hydrogen to the hydroxyl groups of the aldehyde-ammonia to form water, the residue can then unite, with elimination of ammonia, to form the compound $HS\cdot C\lessdot\begin{array}{l}NH\\NH\cdot N(C_2H_4)_2\end{array}$. But with substituted thioureas this simultaneous loss of 2H cannot occur, and hence no interaction takes place. The substitution derivatives obtained from the thiocarbimides may be formulated thus:—$HS\cdot C\lessdot\begin{array}{l}NR\\NH\cdot N(C_2H_4)_2\end{array}$, whereby the decomposition by water becomes intelligible; the molecule readily breaks down at the point of junction of the two directly linked nitrogen atoms; ammonia and 2 mols. of aldehyde result, and the residue is a monosubstituted thiourea $HS\cdot C\lessdot\begin{array}{l}NR\\NH_2\end{array}$. From Nencki's compound, or its homologue, by a precisely similar interaction, thiourea itself, $HS\cdot C\lessdot\begin{array}{l}NH\\NH_2\end{array}$, would result.

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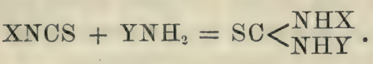
XLIX.—*Isomerism amongst the Substituted Thioureas.*

By Augustus E. Dixon, M.D., Professor of Chemistry, Queen's College, Cork.

It has been established in every case hitherto recorded that the product resulting from the combination of a given thiocarbimide XNCS with a given primary amine YNH_2 is identical with that obtained by the action of the thiocarbimide YNCS upon the amine XNH_2.

This admits of explanation most simply by the supposition that the resultant compound is symmetrical, in which case the interaction leading to its formation is expressed thus:—



$$XNCS + YNH_2 = SC{<}\begin{smallmatrix}NHX\\NHY\end{smallmatrix}.$$

But, on the other hand, evidence is rapidly accumulating,* which points to the view that thiourea itself, together with its mono- and tri-substitution derivatives, are unsymmetrical compounds of the type $HN{:}C{<}\begin{smallmatrix}NH_2\\SH\end{smallmatrix}$.

If, therefore, the di-substitution derivatives are similarly constituted, the production of identical compounds under the above circumstances would involve the shifting of the groups in the molecule at the moment of its formation, so as to allow of the former assuming a definite position of maximum stability. This view is, however, by no means free from difficulty, for it will be shown later on, that amongst the tri-substituted thioureas, which are produced similarly from the thiocarbimides and secondary amines, no such mobility is observed; and though this of course does not exclude the possibility of such change in the case of di-substituted compounds, it renders it somewhat improbable. From these difficulties an escape has recently been sought in the idea of tautomerism; the compounds may be symmetrical when in the solid state, whilst the three forms $SC{<}\begin{smallmatrix}NHX\\NHY\end{smallmatrix}$, $XN{:}C{<}\begin{smallmatrix}NHY\\SH\end{smallmatrix}$, and $YN{:}C{<}\begin{smallmatrix}NHX\\SH\end{smallmatrix}$ may all coexist in solution (Foerster, *Ber.*, **21**, 1872).

Though in numerous instances the di-substituted thioureas have been thus prepared by the "cross method" above mentioned, it is remarkable that, so far, no investigation appears to have been carried out with the view of ascertaining whether the tri-substituted derivatives produced in like manner would be identical or isomeric.

In a paper recently communicated to this Society ("New Benzylic Derivatives of Thiocarbamide," Trans., 1891, 551), I incidentally described two methylphenylbenzyl compounds which were isomeric, but the two corresponding ethylphenylbenzyl derivatives presented so close a resemblance, that it was impracticable, on the data then acquired, to predicate their identity or otherwise. Some further information has since been accumulated bearing on the subject in question, though unexpected experimental difficulties have prevented its being as complete as was originally hoped. I now beg to communicate the results.

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* See *e.g.*, Storch (Abstr., 1891, 548); Reynolds (Trans., 1891, 394); Dixon (Trans., 1892, 509), and Bertram (*post*, p. 543).

Isomerism is obviously impossible amongst compounds produced from thiocarbimides and secondary amines where all three radicles are identical. Where two are identical, two isomers can theoretically be formed, whilst where all three differ, three isomeric forms are possible. Thus, assuming for the moment the resultant product to be constituted on the symmetrical type:—

A.—

$$\text{I. } \mathrm{CSNX} + \mathrm{NHY_2} = \mathrm{SC}{<}^{\mathrm{NY_2}}_{\mathrm{NHX}},$$

$$\text{II. } \mathrm{CSNY} + \mathrm{NHXY} = \mathrm{SC}{<}^{\mathrm{NXY}}_{\mathrm{NHY}};$$

or, if unsymmetrical—

$$\text{I. } \mathrm{CSNX} + \mathrm{NHY_2} = \mathrm{XN{:}C}{<}^{\mathrm{NY_2}*}_{\mathrm{SH}},$$

$$\text{II. } \mathrm{CSNY} + \mathrm{NHXY} = \mathrm{YN{:}C}{<}^{\mathrm{NXY}}_{\mathrm{SH}}.$$

B. Symmetrical—

$$\text{I. } \mathrm{XNCS} + \mathrm{NHYZ} = \mathrm{SC}{<}^{\mathrm{NYZ}}_{\mathrm{NHX}},$$

$$\text{II. } \mathrm{YNCS} + \mathrm{NHXZ} = \mathrm{SC}{<}^{\mathrm{NXZ}}_{\mathrm{NHY}},$$

$$\text{III. } \mathrm{ZNCS} + \mathrm{NHXY} = \mathrm{SC}{<}^{\mathrm{NXY}}_{\mathrm{NHZ}}.$$

If the type be unsymmetrical, three isomeric derivatives are similarly possible.

A. TRI-SUBSTITUTED THIOUREAS CONTAINING TWO DIFFERENT RADICLES.

Phenylthiocarbimide and Dimethylamine.

Molecular proportions of the above constituents were separately dissolved in alcohol, and the solutions mixed; interaction rapidly took place with evolution of heat, and, on cooling, the whole solidified to a crystalline mass which, when drained and recrystallised from alcohol, yielded long, white, pointed prisms melting at 134—135° (uncorr.) without decomposition.

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* That the sulphur is not attached to a compound radicle in these substances is shown by the fact that, on desulphurisation by metals, a metallic sulphide, and not a mercaptide, is produced.

A sulphur determination showed the product to consist of the expected phenyldimethylthiourea.

0·2300 gram of substance, dried over sulphuric acid, yielded 0·2934 gram $BaSO_4$.

	Calculated for $C_9H_{12}N_2S$.	Experiment.
S........	17·79 per cent.	17·53 per cent.

The substance is moderately soluble in boiling water, very sparingly in cold, very freely in hot alcohol, much less so in cold.

Its aqueous solution is not desulphurised by boiling with an alkaline solution of lead. Silver nitrate gives no precipitate, but the mixture gradually blackens even when cold, and after some time a very brilliant silver sulphide mirror forms. With ammoniacal silver nitrate, a white, curdy precipitate falls; this is stable in the cold, and is only slowly blackened even on boiling.

On boiling with aniline, the solid evolves dimethylamine, and the residue, on treatment with dilute hydrochloric acid, yields a crystalline mass consisting of thiocarbanilide :—

$$CSN_2H(CH_3)_2{\cdot}C_6H_5 + C_6H_5{\cdot}NH_2 = CSN_2H_2(C_6H_5)_2 + NH(CH_3)_2.$$

The compound above described is accordingly isomeric with Gebhardt's "symmetrical dimethylphenylthiourea, $SC{<}^{NH\cdot CH_3}_{N(CH_3)\cdot C_6H_5}$" (*Ber.*, **17**, 3037), obtained from methylthiocarbimide and methylaniline in the form of vitreous, transparent prisms melting at 114°, and decomposed by boiling aniline, with formation of methylamine, methylaniline, and thiocarbanilide.

Attempts were made to obtain other analogous compounds, but unsuccessfully. Gebhardt (*Ber.*, **17**, 3038) records his failure to obtain from diethylamine and phenylthiocarbimide a phenyldiethylthiourea; I can corroborate his statements as regards the difficulty of obtaining a solid product; in my experiments hot, strong, alcoholic solutions were first employed, and later on dilute and strongly cooled; the product being in every case a tenacious, uncrystallisable oil.

No better success attended the attempt to prepare an isomer from ethylthiocarbimide and ethylaniline; these substances failed to combine when heated together for three hours at 100°. Another hour's heating at 130—135° somewhat deepened the colour of the mixture, which still smelt pungently of the unchanged thiocarbimide; and after successive fruitless heatings at 155° and 160°, the temperature was raised for an hour to 230°. Complete decomposition was the result; the contents of the tube formed a blackish-red oil, whilst combustible gas escaped on opening it, and this, as well as the oily residue, smelt strongly of mercaptan.

B. Tri-substituted Thioureas Containing Three Different Radicles.

As recorded in my paper on benzylic derivatives of thiocarbamide (*loc. cit.*), methylthiocarbimide and benzylaniline yield a trisubstitution derivative melting at 121°, whilst from benzylthiocarbimide and methylaniline a substance is obtained of the same ultimate composition, but melting at 85°. Here the isomerism in two of the three possible cases is sufficiently obvious; but this was by no means the case where the corresponding ethylated compounds were concerned.

From benzylthiocarbimide and ethylaniline on the one hand, and from ethylthiocarbimide and benzylaniline on the other, substances were obtained melting at 91°, agreeing in ultimate composition; in the main, in reactions; and also in general appearance; the only point of distinction definitely noted being that the long prisms of the former were oblique, whilst those of the latter were somewhat broader, and rectangular. But no more material differences were observed, and under an ordinary, not very minute examination, the products might readily have passed for identical.

A subsequent investigation has revealed the fact that, in spite of their close resemblance, these substances are really isomeric.

Action of Ammonia on the Benzylthiocarbimide-Ethylaniline Compound.—The benzylthiocarbimide derivative was sealed up with a considerable excess of alcoholic ammonia, and heated for an hour at about 100°. On removal and exposure to air, the contents of the tube soon began to deposit rosettes of white needles; when the separation was complete, the latter were collected, recrystallised from alcohol, and examined. They were somewhat sparingly soluble in boiling water, insoluble in cold; slowly desulphurised by boiling with alkaline solution of lead; melted between 161° and 162°, and consisted obviously of benzylthiourea. Melting point of the latter (Trans., 1892, 553), 161—162°. The filtrate from the original crop of needles, on further concentration by exposure to air, began to turn green, and, when poured into water, gave a precipitate consisting of oily drops, possessing the characteristic odour of ethylaniline. Under the action of alcoholic ammonia, therefore, the decomposition runs as follows:—

$$CSN_2H(C_7H_7)(C_2H_5)\cdot C_6H_5 + NH_3 = CSN_2H_3\cdot C_7H_7 + C_6H_5\cdot NH\cdot C_2H_5.$$

Action of Ammonia on the Ethylthiocarbimide-Benzylaniline Compound.—On similarly heating the above ethylthiocarbimide derivative with alcoholic ammonia, it was scarcely attacked—a fact in itself suggestive of isomerism. Heating for four hours at 105—110° also failed to induce any material decomposition; this was effected, however, by heating for about an hour at 125°; at the end of this time the temperature was further pushed for a few minutes to 140°. The product was a brownish liquid, from which, on standing, no solid matter separated. Excess of water was then added, whereupon a brown oil was precipitated, and this, after standing for some hours, solidified. The solid product, when heated alongside another tube containing pure benzylaniline, and attached to the same thermometer, melted at the same temperature as the latter, viz., 38°.* The aqueous liquid from which the oil had been separated was concentrated by evaporation, the brownish solid thus obtained drained off, redissolved in water, treated with animal charcoal, and the filtrate allowed to crystallise slowly. Tufts of almost colourless needles were thus obtained, freely soluble in water and alcohol, moderately readily desulphurised by alkaline lead solution, and melting at 110—112°. An analysis was considered unnecessary, as the substance was evidently ethylthiourea (m. p. 113°). In this case, therefore, the action of alcoholic ammonia leads to a decomposition different from that previously described, thus:—

$$CSN_2H(C_2H_5)(C_6H_5)\cdot C_7H_7 + NH_3 = CSN_2H_3\cdot C_2H_5 + C_6H_5\cdot NH\cdot C_7H_7,$$

and the isomerism of this with the preceding compound is hence clearly established.

It remained now to be learned, from further experiments, whether the third possible isomeric form of ethylphenylbenzylthiourea would be produced under the conditions which might be expected to lead to its formation.

Phenylthiocarbimide and Ethylbenzylamine.

Ethylbenzylamine, prepared according to Kraft's method (*Ber.*, **23**, 2781), by the action of benzyl chloride on ethylamine, was mixed, in ethereal solution, with phenylthiocarbimide, and the mixture set aside. After a month, crystals began to appear, and rapidly formed, until at last the whole became solid. The product was broken up, drained on the filter-pump, washed with spirit, and the now colourless residue dissolved in boiling alcohol; from this, it separated, on cooling, in tufts of vitreous prisms, which, when seen in mass, were snow-white.

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* The melting point ordinarily given for this compound, 32°, is too low.

A portion was dried over sulphuric acid, and the sulphur estimated.

0·2115 gram of substance gave 0·1832 gram $BaSO_4$.

	Calculated for $CSN_2H(C_6H_5)(C_2H_5)\cdot C_7H_7$.	Experiment.
S........	11·86 per cent.	11·90 per cent.

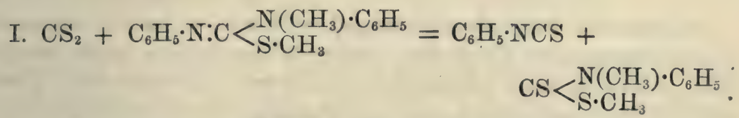
Phenylethylbenzylthiourea is very sparingly soluble in boiling water, insoluble in cold. It is apparently indefinitely soluble in boiling alcohol, though only moderately so in cold; very freely in benzene, chloroform, and carbon bisulphide; moderately in ether. Its melting point lies between 94° and 95°.

On the addition of silver nitrate to the alcoholic solution, no change appears to occur for a few seconds; then the mixture suddenly blackens. Ammoniacal silver nitrate throws down a white, curdy precipitate, which is stable in the cold. On warming carefully, the precipitate disappears, yielding a clear, colourless solution; the latter, when heated to near its boiling point, decomposes with separation of silver sulphide. The substance is also gradually desulphurised by continued boiling with alkaline solution of lead.

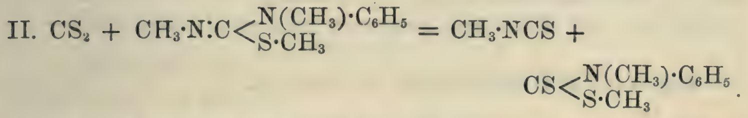
This compound is isomeric with the two preceding, and the suggestion of group mobility in these cases is therefore distinctly negatived; for convenience of comparison, a short table is appended, showing the chief points of difference:—

	EtNCS + BzNHPh.	BzNCS + EtNHPh.	PhNCS + EtNHBz.
Melting point	90·5—91°.	90—91°.	94—95°.
Silver nitrate	Mixture slowly becomes yellow, and then reddish, and lastly black	Mixture slowly becomes grey, passing gradually to black	Mixture colourless for a few seconds, then suddenly blackens.
Ammoniacal silver nitrate	White, curdy pp., blackened at once on heating	White, curdy pp. Mixture partly clears on heating, and becomes yellow; then rapidly blackens	White, curdy pp., dissolving on heating to colourless solution. Latter blackens only when heated to near its boiling point.
Alk. lead solution .	Not desulphurised	Not desulphurised	Slowly desulphurised.
Action of ammonia	Yields $C_7H_7\cdot NHPh + CSN_2H_3Et$	Yields $EtNHPh + CSN_2H_3\cdot C_7H_7$	—

With respect to the structure of these tri-substituted thioureas, it appears highly probable that they are unsymmetrical. For, in the first place, the fact that the thiocarbimides unite readily with secondary amines, but not with the tertiary, seems to point to a special function for the fourth hydrogen atom in the higher derivatives, which is somewhat difficult to reconcile with their symmetrical constitution. And, secondly, it has recently been shown by Bertram (*Ber.*, **25**, 57) that the basic substance produced by the addition of alkali to the compound of methyl iodide with methyl diphenylthiourea (from phenylthiocarbimide and methylaniline) yields, on treatment with carbon bisulphide, the methyl salt of methylphenyldithiocarbamic acid, a substance which results equally from the action of carbon bisulphide on the compound $CH_3{\cdot}N{:}C{<}\begin{array}{l}N(CH_3){\cdot}C_6H_5\\ S{\cdot}CH_3\end{array}$, obtained by successive methylations of phenylthiourea. These interactions are thus explained :—

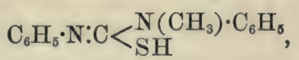


$$\text{I. } CS_2 + C_6H_5{\cdot}N{:}C{<}\begin{array}{l}N(CH_3){\cdot}C_6H_5\\ S{\cdot}CH_3\end{array} = C_6H_5{\cdot}NCS + CS{<}\begin{array}{l}N(CH_3){\cdot}C_6H_5\\ S{\cdot}CH_3\end{array}.$$



$$\text{II. } CS_2 + CH_3{\cdot}N{:}C{<}\begin{array}{l}N(CH_3){\cdot}C_6H_5\\ S{\cdot}CH_3\end{array} = CH_3{\cdot}NCS + CS{<}\begin{array}{l}N(CH_3){\cdot}C_6H_5\\ S{\cdot}CH_3\end{array}.$$

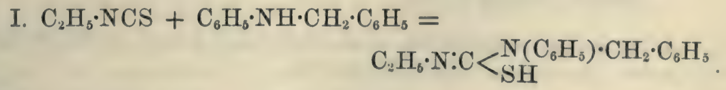
As the sulphur atom is known to be linked to the alkyl radicle introduced by the action of an alkylogen on the thioureas (for a mercaptide is produced on desulphurisation of the product by certain metals), whilst in the isomeric forms produced by the interaction of amines with thiocarbimides it is not so linked, the inference is strong that the methyldiphenylthiourea above mentioned is of the form



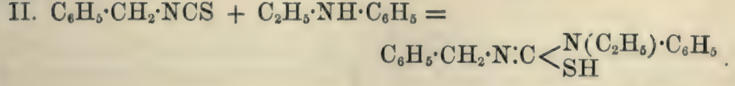
$$C_6H_5{\cdot}N{:}C{<}\begin{array}{l}N(CH_3){\cdot}C_6H_5\\ SH\end{array},$$

which, uniting with methyl iodide, exchanges its SH hydrogen for the methyl group to yield the compound formulated in equation I.

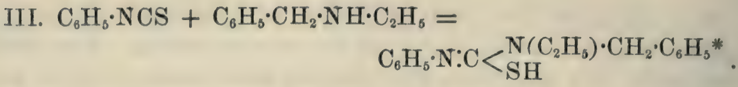
The interactions leading to the formation of the isomeric ethylphenylbenzylthioureas may, therefore, be expressed as follows :—



$$\text{I. } C_2H_5{\cdot}NCS + C_6H_5{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5 = C_2H_5{\cdot}N{:}C{<}\begin{array}{l}N(C_6H_5){\cdot}CH_2{\cdot}C_6H_5\\ SH\end{array}.$$

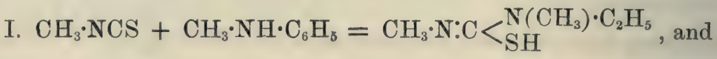


$$\text{II. } C_6H_5{\cdot}CH_2{\cdot}NCS + C_2H_5{\cdot}NH{\cdot}C_6H_5 = C_6H_5{\cdot}CH_2{\cdot}N{:}C{<}\begin{array}{l}N(C_2H_5){\cdot}C_6H_5\\ SH\end{array}.$$

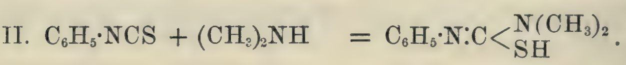


$$\text{III. } C_6H_5{\cdot}NCS + C_6H_5{\cdot}CH_2{\cdot}NH{\cdot}C_2H_5 = C_6H_5{\cdot}N{:}C{<}\genfrac{}{}{0pt}{}{N(C_2H_5){\cdot}CH_2{\cdot}C_6H_5{}^{*}}{SH}.$$

It may here be mentioned that Bertram obtained, by twice methylating phenylthiourea, a compound to which he assigns the formula $HN{:}C{<}\genfrac{}{}{0pt}{}{N(CH_3){\cdot}C_6H_5}{S{\cdot}CH_3}$. The latter is a faintly yellow, basic oil, and is hence isomeric with Gebhardt's methylmethylphenylthiourea (m. p. 114°) and the phenyldimethylthiourea (m. p. 135°), which I have described above. The formation of these substances may be thus represented:—

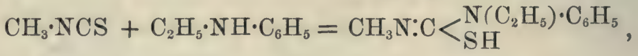


$$\text{I. } CH_3{\cdot}NCS + CH_3{\cdot}NH{\cdot}C_6H_5 = CH_3{\cdot}N{:}C{<}\genfrac{}{}{0pt}{}{N(CH_3){\cdot}C_2H_5}{SH}, \text{ and}$$



$$\text{II. } C_6H_5{\cdot}NCS + (CH_3)_2NH \quad = C_6H_5{\cdot}N{:}C{<}\genfrac{}{}{0pt}{}{N(CH_3)_2}{SH}.$$

Experiments were also conducted with a view to investigate the methylethylphenyl series, but, owing to the failure, after repeated trial, to obtain from ethylthiocarbimide and methylaniline a solid product, they were abandoned. Gebhardt's methylethylphenyl compound (*Ber.*, **17**, 3037) was, however, incidentally produced:—



$$CH_3{\cdot}NCS + C_2H_5{\cdot}NH{\cdot}C_6H_5 = CH_3N{:}C{<}\genfrac{}{}{0pt}{}{N(C_2H_5){\cdot}C_6H_5}{SH},$$

and to his description the following may be added:—

The substance is insoluble in water, and crystallises slowly from alcohol (in which, as he notes, it is extremely soluble) in very large, vitreous rhombohedra; these, after recrystallisation, were obtained quite colourless, and melted at 67—68°. On the addition of silver nitrate to the alcoholic solution, the mixture blackens instantly, and if it be then heated, a mirror forms; with the ammoniacal nitrate, a yellow coloration is produced, slowly changing, first to crimson-red, and passing on then, through deep red, to black. But the solution is not desulphurised, even by prolonged boiling with moderately dilute alkaline lead tartrate.

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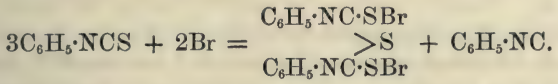
[*] By the successive introduction of one of the three radicles into the SH group, no less than six additional isomers are possible.

L.—*Action of Bromine on Allylthiocarbimide.*

By Augustus E. Dixon, M.D., Professor of Chemistry, Queen's College, Cork.

Chemical literature contains but few references to the action of bromine on thiocarbimides: no investigation as to its action on the paraffinoïd thiocarbimides appears to have been recorded; whilst in the aromatic class the phenyl and paratolyl compounds alone have been examined, and even with regard to phenylthiocarbimide, different observers are not agreed. According to Proskauer and Sell (*Ber.*, **9**, 1262), these substances interact to form a deep, orange-red, solid dibromide, according to the equation:—



$$3C_6H_5\cdot NCS + 2Br = \left.\begin{matrix} C_6H_5\cdot NC\cdot SBr \\ C_6H_5\cdot NC\cdot SBr \end{matrix}\right> S + C_6H_5\cdot NC.$$

Helmers (*Ber.*, **20**, 788), though following their directions, failed to corroborate this statement, the product obtained by him being a solid dibromo-addition compound, $C_6H_5\cdot NCS,Br_2$, which, on exposure to air, loses bromine, yielding $C_6H_5\cdot NCS,Br$ or $(C_6H_5\cdot NCS)_2,Br_2$. From paratolylthiocarbimide, a corresponding unstable derivative, $C_7H_7\cdot NCS,Br_2$, was obtained.

Concerning its action upon allylthiocarbimide, the only fact which seems to have been recorded is that by Aschoff (*J. pr. Chem.*, **4**, 314), to the effect that on the addition of bromine, frothing and evolution of heat occur, a brown resin being produced, nearly insoluble in water; the solution contains sulphuric and hydrobromic acids. In Proskauer and Sell's paper (*loc. cit.*) it is mentioned that by combining bromine with ethyl- and allyl-thiocarbimides respectively, substances are produced similar to that mentioned above, but no experimental evidence in support of this statement is adduced, nor in fact are any data whatever given.

Considering, however, the readiness with which bromine attaches itself to the allyl group, it seemed probable that it would unite with oil of mustard to form a dibromopropylthiocarbimide, thus:—

$$CH_2\colon CH\cdot CH_2\cdot NCS + 2Br = CH_2Br\cdot CHBr\cdot CH_2\cdot NCS.$$

An experimental investigation was therefore undertaken in order to test the correctness, or otherwise, of this view; the results are stated below.

In the earlier experiments, dry air was caused to bubble through a wash-bottle containing bromine, the escaping vapours being led thence into a chloroform solution of allylthiocarbimide, kept cold by means of a freezing mixture. Subsequent experiment, however, showed that the desired combination can be equally well effected by bringing solutions of the constituents together: the following method of operating was found to give the best result.

Allylthiocarbimide was dissolved in about six times its own volume of chloroform, the containing vessel surrounded by a freezing mixture (hydrochloric acid and sodium sulphate), and a molecular proportion of bromine, also well diluted with chloroform, and similarly cooled, allowed to pass in drop by drop from a tap-funnel. The bromine must be added very gradually, and with constant agitation of the thiocarbimide solution, or else the mixture soon becomes turbid from separation of a pasty substance; even when operating in the manner described, a small quantity of reddish, tenacious, unstable oil was produced.

As soon as the bromine came in contact with the mustard oil, a yellowish-red coloration appeared, which did not sensibly deepen as the addition was continued. The bromine was immediately and completely absorbed, and when the process was at an end, the mixture possessed scarcely any odour save that of the chloroform used as solvent. The solution was now decanted from a little oily matter, and most of the chloroform distilled off on the water-bath. A little fuming was noticeable during this process, and the distillate contained a small quantity of hydrobromic acid.

The residue, a bright-yellow oil, was steam-distilled; first some chloroform was rapidly driven off, then a few drops of liquid possessing a sharp, pungent odour, and consisting substantially of unchanged allylthiocarbimide, after which a heavy, strongly refractive oil came slowly over, leaving a trifling quantity of dull-brown semi-solid residue in the distilling flask. The aqueous contents of the latter gave a faint reaction for sulphuric acid.

The oily product was extracted with pure ether, the latter quickly distilled off on the water-bath, and the residue freed from water by standing in contact with calcium chloride. Qualitative examination showed that it contained nitrogen, bromine, and sulphur. A portion was heated for a short time* at 100°, allowed to cool in a vacuum, and analysed.

0·2310 gram of substance gave 11·6 c.c. moist nitrogen, measured at 16·5° and 750·5 mm.

0·8137 gram of substance oxidised by somewhat diluted nitric acid, in presence of $AgNO_3$, gave 1·1638 gram AgBr.

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* Over-long heating must be avoided, for the dry substance soon begins to decompose, giving off fumes of hydrogen bromide.

The filtrate from above yielded 0·706 gram $BaSO_4$.

0·9514 gram of substance yielded 0·8298 gram $BaSO_4$.

These results indicate a dibromo-addition product of allylthiocarbimide:—

	Calculated for $C_3H_5Br_2NCS$.	Experiment.
N.......	5·42 per cent.	5·76 per cent.
Br......	61·71 ,,	60·86 ,,
S.......	12·37 ,,	11·93 .. 11·99 per cent.

The yield, measured only in a single case, amounted to 70 per cent. of the theoretical.

When freshly distilled, the oil is almost colourless, but on drying, becomes yellowish, and on heating to expel the last traces of dissolved ether, the colour deepens to a golden yellow. It has a faint, thiocarbimidic odour, which, on warming, becomes pungent and irritating; the alcoholic solution has a burning taste. At 17°/17°, the sp. gr. was found to be 1·9712.

The substance is practically insoluble in water, easily soluble in strong alcohol, but the amount taken up rapidly diminishes if a more hydrous alcohol be employed; it is freely miscible with ether, chloroform, and benzene.

When treated with a few drops of neutral or ammoniacal silver nitrate, no precipitate forms; but the mixture blackens slowly in the cold or at once on warming. Alkaline solution of lead or freshly precipitated mercuric hydroxide desulphurises it readily on gentle heating.

In the cold, the substance is quite stable, a specimen kept for nearly a year showing no sign of alteration; in this respect, therefore, it presents a marked contrast to the unstable compounds obtained by the combination of bromine with phenyl- and paratolylthiocarbimides. Its properties, in fact, point clearly to its being a thiocarbimide (dibromopropylthiocarbimide), and any possible doubt with regard to this is removed by a study of its action on aniline (*vide infra*).

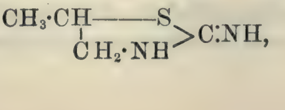
On distillation (at atmospheric pressure) the oil darkens, effervesces, and is completely decomposed: hydrogen bromide and sulphuretted hydrogen are evolved, a smell resembling that of diallyl sulphide is produced, a trace of white, pasty solid adheres to the wall of the condensing tube, and a carbonaceous residue is left in the distilling flask.

If bromine be directly added to allylthiocarbimide rather violent action occurs; the bromine is at once decolorised, and the product separates into two layers. The upper is colourless, and when poured into water, yields a milky emulsion, the clear filtrate from which contains much sulphuric and hydrobromic acids. The lower is reddish-yellow, and consists of the above-described brominated thiocarbimide in an impure condition.

Action of Nascent Hydrogen.—When treated with tin and hydrochloric acid the oil slowly dissolved; the escaping gas smelt faintly of sulphuretted hydrogen, and blackened "lead paper." When the action was complete, excess of potash was added, and the mixture distilled. A strongly alkaline, unpleasantly smelling liquid came over, which, on the addition of hydrochloric and platinic chloride, gave a yellow precipitate. The substance was presumably propylamine, but owing to want of material it was not examined in detail.

Action of Ammonia.—This could, theoretically, give rise to the formation of a dibromopropylthiourea, $CH_2Br\cdot CHBr\cdot CH_2\cdot N{:}C{<}{\substack{NH_2\\SH}}$. Paal and Heupel (*Ber.*, **24**, 3039), however, found that by the action of dibromopropylamine hydrobromide on potassium thiocyanate, "a thick, colourless syrup was produced, from which nothing crystallisable could be obtained." On similarly attempting to combine dibromopropylthiocarbimide with alcoholic ammonia, ammonium bromide was formed together with a smeary, tenacious, basic syrup, which could not be obtained sufficiently pure for analysis. Better success attended the use of aniline.

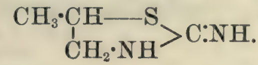
Action of Aniline.—This substance was caused to act on the thiocarbimide with the view, if possible, of obtaining dibromopropylphenylthiourea, $CS{<}{\substack{NH\cdot CH_2\cdot CHBr\cdot CH_2Br\\NH\cdot C_6H_5}}$. It has been shown, however, by Gabriel and others (see Gabriel, *Ber.*, **22**, 1140; Prager, *ibid.*, **22**, 2992; Hirsch, *ibid.*, **23**, 964; Avenarius, *ibid.*, **24**, 260); that certain mono- and di-substituted thioureas containing monobrominated paraffin radicles very readily undergo change into basic substances by loss of the elements of hydrogen bromide; and for this reason it seemed somewhat improbable that the substance formulated above would be obtained as such. The mechanism in the case of mono-substitution derivatives is explained as follows:—When, for example, β-bromopropylamine is combined with potassium thiocyanate, the resultant is probably a brominated thiourea, $CSN_2H_3\cdot C_3H_6Br$, which, losing hydrogen bromide, yields the ring compound

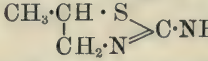
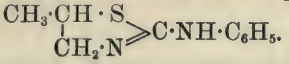


$$\begin{array}{l}CH_3\cdot CH\text{———}S\\ \quad\;\; CH_2\cdot NH\end{array}{>}C{:}NH,$$

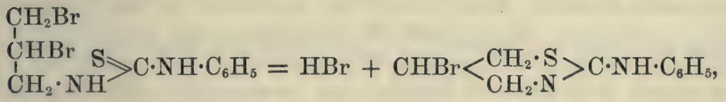
a substance which can also be prepared from allylthiourea itself by heating it with hydrobromic (or hydrochloric) acid :—

I. $CSN_2H_3\cdot CH_2\cdot CH{:}CH_2 + HBr = CSN_2H_3\cdot CH_2\cdot CHBr\cdot CH_3.$

II. $CSN_2H_3\cdot CH_2\cdot CHBr\cdot CH_3 = HBr +$ 
$$\begin{array}{l}CH_3\cdot CH\text{---}S\\ \quad |\\ \quad CH_2\cdot NH\end{array}\!\!>C{:}NH.$$

It is admitted that though the above formula appears the most probable, the structure may possibly be  $\begin{array}{l}CH_3\cdot CH\cdot S\\ \quad |\\ \quad CH_2\cdot N\end{array}\!\!\geqslant C\cdot NH_2$; and in the case of substitution products the latter has been established by Prager (*loc. cit.*) for aromatic, and by Avenarius (*loc. cit.*) for alkyl derivatives. Thus from allylphenylthiourea "*n*-phenylpropylene-ψ-thiourea" was obtained,  $\begin{array}{l}CH_3\cdot CH\cdot S\\ \quad |\\ \quad CH_2\cdot N\end{array}\!\!\geqslant C\cdot NH\cdot C_6H_5$.

By the combination, therefore, of dibromopropylthiocarbimide with aniline, it might be expected that dibromopropylphenylthiourea would only occur as an intermediate product from which, by loss of hydrogen bromide, a brominated derivative of *n*-phenylpropylene-ψ-thiourea should result :—


$$\begin{array}{l}CH_2Br\\ |\\ CHBr\quad S\\ |\\ CH_2\cdot NH\end{array}\!\!\geqslant C\cdot NH\cdot C_6H_5 = HBr + CHBr\!<\!\begin{array}{l}CH_2\cdot S\\ CH_2\cdot N\end{array}\!\!>C\cdot NH\cdot C_6H_5,$$

or possibly the second bromine atom might also be removed. The experiment was carried out as follows :—

Theoretical quantities of base and thiocarbimide were dissolved in alcohol,* and the solutions mixed. No perceptible rise of temperature occurred; the solution was therefore heated to its boiling point, whereupon it became pink, and the odour of its constituents was lost. On evaporating the solvent at a gentle heat, a pinkish-red liquid was obtained, which became syrupy on cooling : this was dissolved in dilute hydrochloric acid (in which it is very freely soluble), and the solution treated with excess of caustic potash ; a heavy, dark-brown, sticky oil mixed with a little solid matter precipitated at once. The oil was drawn off, and after some days began to solidify ; when solid, the mass was broken up and twice recrystallised from alcohol. The substance was thus obtained in tufts of pure white crystals melting between 103° and 104° (uncorr.). Analysis gave the following data :—

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* If the constituents be directly mixed, violent action occurs, and the product is a deep-red, tenacious mass.

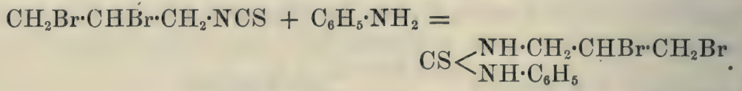
0·3143 gram of substance gave 0·2213 gram AgBr and 0·2795 gram $BaSO_4$.

0·1203 gram of substance gave 10·8 c.c. moist nitrogen, measured at 18° and 762·5 mm.

These results are in accordance with the formula $C_{10}H_{11}BrN_2S$:—

	Calculated.	Experiment.
N........	10·32 per cent.	10·40 per cent.
Br	29·38 ,,	29·96 ,,
S	11·78 ,,	12·22 ,,

and the formation of the compound may be thus represented :—



$$CH_2Br\cdot CHBr\cdot CH_2\cdot NCS + C_6H_5\cdot NH_2 = CS{<}\begin{matrix}NH\cdot CH_2\cdot CHBr\cdot CH_2Br\\ NH\cdot C_6H_5\end{matrix}.$$

Dibromopropylphenylthiourea is, however, not obtained as such under the above conditions : a molecule of hydrogen bromide splits off, leaving $C_{10}H_{11}BrN_2S$.

Since the bromine atom in the γ-position is more easily removable than that in the β-position (see Paal, *Ber.*, **24**, 4253), it may be assumed, at least provisionally, that the former is eliminated (see also Andreasch, *Monatsh.*, **5**, 33), and the structure of the compound represented thus :—$CHBr{<}\begin{matrix}CH_2\cdot N\\ CH_2\cdot S\end{matrix}{>}C\cdot NH\cdot C_6H_5$, that is, a brominated phenyl derivative of Gabriel and Lauers (*Ber.*, **23**, 94), "trimethylene-ψ-thiourea."

It may here be noted that the above behaviour of a halogen derivative of a thiocarbimide under the influence of bases is not exceptional. v. Hofmann obtained (*Ber.*, **12**, 1130) by the action of aniline on chlorphenylthiocarbimide a halogen-free substance, "*Anilidosenföl*," which, on further examination (*ibid.*, **13**, 20), proved to be a compound of the form $C_6H_4{<}\begin{matrix}N\\ S\end{matrix}{>}C\cdot NH\cdot C_6H_5$; this case is a parallel, in the aromatic class, to the one described.

n-Phenylbromotrimethylene-ψ-thiourea is insoluble in water, freely soluble in hot alcohol, moderately in cold. Its alcoholic solution, on the addition of ammoniacal silver nitrate, yields no precipitate; neither is it desulphurised by ordinary treatment with alkaline lead solution: the latter mixture blackens only when boiled down almost to dryness.

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LI.—*Estimation of Slag in Wrought Iron.*

By A. E. Barrows, Student in the Metallurgical Laboratory, Mason College, and Thomas Turner.

In recent communications on the manufacture of wrought iron (*Journ. Iron and Steel Inst.*, 1891, and *Proceedings S. Staff. Inst. Iron and Steel Works Managers*, 1892), one of us has drawn attention to the fact, long known by practical men, that pig iron comparatively rich in elements such as carbon, silicon, and phosphorus yields a greater weight of puddled iron than is obtained when pig iron of greater chemical purity is employed. This increased yield is due to the reducing action of the nonmetallic elements on the oxidising fettling and slag of the furnace. But it is also noticed that puddled iron made from impure pigs loses more in weight when reheated and rolled into merchant iron than is the case with puddled iron made from pure materials. It has, therefore, been suggested that part, if not the whole, of the increase of weight noticed in the first instance is due to the presence of an excess of intermingled slag in the case of iron made from impure or "common" pigs. The object of the present enquiry was to determine, if possible, the condition in which the impurities exist in the case of the respective varieties of wrought iron.

For the purpose of this enquiry, four special preparations of wrought iron were made at the Bloomfield Iron Works, Staffordshire, with which one of us is connected. The samples were prepared in the ordinary course of business in order to as nearly as possible represent what actually occurs in practice; but a mixture of cast iron of known composition was employed, and the ordinary process of rolling was modified so as to avoid the admixture of other iron.

In the first case, the furnace was fettled as usual for "best" iron, and a charge of Staffordshire "all mine" pig iron of the usual weight (4 cwt. 1 qr. 18 lbs.) was puddled by an experienced workman in the ordinary manner. The product, afterwards referred to as "best puddled bar," was cut up, reheated, and rolled into medium thick sheet, without the addition of any scrap iron in the pile. This gave the sample of "best sheet iron" for subsequent examination.

For the "common" iron, a special mixture of Staffordshire "part mine" and Northamptonshire pig iron was employed, the usual fettling for this class of iron was used, and the products were "common puddled bar" and (after reheating and rolling as before without adding scrap) "common sheet iron."

The charge for "best" iron would contain not more than 0·5 per cent. of phosphorus and 1·5 per cent. of silicon, whilst for "common" iron the phosphorus would amount to 1·75 per cent., and the silicon to about 2·5 per cent. The average yield of the best iron, as deduced from regular weighings at the works, was 4 cwt. 0 qr. 17 lbs., while the yield of common iron was 4 cwt. 1 qr. 17 lbs., showing a difference of 28 lbs. or 5·7 per cent. in favour of the common iron. The loss in reheating the two varieties of puddled bar and rolling down into sheets, as deduced from rolling of rough sheets over a lengthened period, was between 1 and 1·5 per cent. in favour of the best iron; the net result being about 4·5 per cent. in favour of the common iron, as obtained from weighings at the works. These results do not support the view that iron made from impure pigs retains any considerable quantity of slag over and above that retained by metal made from pure materials.

The samples were examined as to their content of carbon, silicon, and phosphorus, which are the important constituents for the purpose of this enquiry. The average of a number of closely concordant experiments was as follows :—

	Best.		Common.	
	Puddled bar.	Sheet.	Puddled bar.	Sheet.
Carbon	0·06	0·035	0·045	0·032
Silicon	0·228	0·168	0·275	0·221
Phosphorus	0·178	0·175	0·589	0·390

From these numbers it will be seen that the common iron contained slightly less carbon, rather more silicon, and much more phosphorus than the best. The silicon and phosphorus taken together amounted to 0·406 in the best iron and 0·864 in the common, or more than double as much in one case as in the other, whilst the loss in reheating and rolling was 0·063 and 0·253 per cent. respectively. So far as we are aware, it is not possible from the chemical analysis to calculate the amount of slag lost during reheating. Thus, if the loss of silicon in common iron, that is, 0·054 per cent., be calculated into slag on the assumption that tap cinder contains at least one-eighth of its weight of SiO_2, the loss of slag would be 0·92 per cent.; whilst calculating from the phosphorus lost, namely, 0·199 per cent., and remembering that the final cinder usually contains only about one-fiftieth of its weight of phosphorus, the weight of slag lost would be 9·95 per cent. The one result is thus ten times as great as the other.

The loss of silicon was practically identical in the two samples on reheating, being 0·06 per cent. with the best iron and 0·054 in the common. On the other hand, the phosphorus was reduced 0·199 per cent. in the common iron, and only 0·003 per cent. in the best. If this difference of phosphorus, 0·196 per cent., be assumed to be eliminated as phosphate with the formula $Fe_3(PO_4)_2$, it would correspond to an *additional* loss for common iron of 1·13 per cent., which agrees so well with that actually observed in practice as to justify the suggestion that the extra loss is due not to the elimination of a greater quantity of slag corresponding to tap cinder, but to the separation of phosphate of iron approaching in composition to ferrous phosphate.

In order to settle, if possible, the exact nature of the changes which take place during the conversion of puddled bar into finished iron, we conducted a number of experiments on the estimation of slag, and of this more strictly chemical subject the rest of our paper will treat. This estimation is rendered difficult by the fact that the slag usually consists of easily decomposable silicates which are attacked by very dilute mineral acids, and even, as Eggertz has shown, by organic acids. The great difficulty, therefore, has been to obtain a solvent for the metal which shall leave the slag unattacked.

In 1872 Mr. Snelus (*Journ. Iron and Steel Institute*, 1872, 258), after attempting a mechanical separation of slag from wrought iron, calculated the amount of slag from the amount of titanium left in the finished iron. In this case the original metal was free from titanium, but the fettling and slag contained a considerable proportion. An estimation was also made by remelting puddled bar in a plumbago crucible in a Siemens' furnace and noting the loss of weight. Such methods were, however, as Mr. Snelus was himself careful to explain, only used for want of a better process, and could but yield uncertain results.

In a previous paper (Trans., **45**, 262), one of us has given an account of some determinations of slag in cast iron by means of the chlorine process originally suggested by Wöhler. It was natural, therefore, that we should, in the first place, apply the same convenient process to wrought iron, especially as the method is recommended by Blair in his recent excellent book, *The Chemical Analysis of Iron*, p. 71, where a detailed description of the analysis is given. A more convenient, and in some respects a more accurate, modification is also given by one of us in the paper above mentioned.

We were, however, surprised to find, on performing the analysis, that the slag obtained by this method varied in colour from bright red to nearly white, according to whether the volatilisation of the iron was rapidly or slowly performed, and we never, on any occasion, obtained a residue of the characteristic dark-grey colour of the tappings obtained when the puddled ball is removed from the furnace in puddling. The weight of residue obtained also varied considerably, and it was only by working in precisely the same way, in different analyses, that the results bore any resemblance to each other. The following figures give the mean values of the numbers we ultimately adopted :—

	Best.	Common.
Bar. Slag per cent.......	1·85	2·27
Sheet. Slag per cent.	1·46	1·97
Loss...............	0·39	0·30

Further experiments were now undertaken to determine the cause of the untrustworthy character of these results.

Half a gram of finely-powdered slag, separated from the puddled ball during manufacture, and presumably the same as that in the ball itself, was heated in a stream of purified chlorine just as in performing an actual analysis, the object being to ascertain whether the slag was attacked by chlorine. On raising the temperature to a low-red heat, a very marked action occurred, and ferric chloride was rapidly volatilised. In a few moments the reaction nearly ceased, and, on cooling and examining the tube, the sample was found to have lost considerably in weight, while the residue was red or purple in colour, and the whole of the iron was converted into the ferric condition. On replacing the boat in the tube, and continuing heating at the same temperature, scarcely any action was observed; but on raising the temperature to full redness, the whole of the iron was gradually volatilised, and a nearly white residue, which was only 26 per cent. by weight of the original slag, remained. A sample of powdered blast furnace slag from the Clarence Iron Works, on the other hand, when heated in a similar manner, was not attacked by chlorine, and even after prolonged heating it was found that 0·5 gram of slag had only increased in weight to 0·5008 gram. These experiments apparently showed that the chlorine process was quite trustworthy for the determination of slag in cast iron, for which purpose it had been previously employed by one of us, although for some reason the process was unsuited for slags containing any considerable proportion of ferrous oxide.

As it was suggested that the action observed might be due to hydrogen chloride present in the chlorine, the apparatus was at this stage overhauled so as to ensure the removal of all but a minute trace of hydrogen chloride, but the result was not at all affected by this alteration; and the sharpness, we might almost say the violence, of the action precludes the suggestion that it is due to the influence of a minute trace of impurity. It was also proved that tap cinder, when heated in a current of hydrogen chloride, was not attacked except at a high temperature, and then a beautiful sublimate of ferrous chloride, in the form of pearly-white flakes, was obtained.

As we were unprepared to find that an oxidised compound of iron should be attacked by chlorine in this manner, and as we do not remember to have seen any observation of a similar character, we endeavoured to determine the nature of the reaction which took place. For this purpose a large number of iron ores were examined, including hydrated and anhydrous peroxides, magnetites, and carbonates. The ores consisting of ferric oxide did not exhibit the first reaction at a low temperature, but with prolonged heating to a high temperature in a current of chlorine, the iron was very slowly volatilised as ferric chloride. On the other hand, all the compounds containing iron in the ferrous condition gave a copious sublimate of ferric chloride when heated to very low redness in chlorine, and the residue in the boat was completely converted into the ferric condition. The residue contained no iron salts soluble in water. Afterwards, with higher temperature and longer heating, the other reaction was noticed. But as some differences were observed in the behaviour of the natural materials from various sources, it was thought advisable to study the action further with some samples of tap cinder, as being more nearly like the slag under examination.

Six samples of tap cinder of known composition were selected for examination; in each case, half a gram of the sample was used in the experiment, and the material was heated in chlorine in a porcelain boat, at a low-red heat, until the first sharp reaction was completed.

The results obtained are given in the following table, and the theoretical loss is calculated according to the equation—

$$3FeO = Fe_2O_3 + Fe,$$

the iron being volatilised as $FeCl_3$ after combination with chlorine.

Expt.	FeO in slag.	Weight taken.	Residue obtained.	Percentage loss.	
				Found.	Theory.
1	59·83	0·5	0·4206	15·88	15·55
2	59·91	0·5	0·4217	15·66	15·58
3	63·96	0·5	0·4168	16·64	16·63
4	64·86	0·5	0·4191	16·18	16·86
5	67·46	0·5	0·4093	18·14	17·54
6	68·46	0·5	0·405	19·00	17·79

When it is remembered that if the temperature be unduly high during the combustion, the second action, leading to loss of ferric oxide, begins to be manifested, and also that tap cinder is apt to contain a little metallic iron, in spite of efforts to separate this during the preparation of the sample, we think that the above results fully justify the equation given. It may, perhaps, be well to point out that the equation

$$4FeO = Fe_3O_4 + Fe$$

would require a loss of only 11·58 per cent. in sample 1 against 15·88 per cent. observed. The residue, also, is not attracted by a magnet, and is red or purple in colour.

The equation just given is similar to that representing the action observed by Deville (*Compt. rend.*, **53**, 199), who obtained magnetic oxide by passing a slow stream of hydrogen chloride over ferrous oxide: in the case of chlorine, however, the action is apparently of a different character.

Sodium Copper Chloride Method.

As the chlorine process was thus proved to yield results which are low and irregular, we conducted a number of experiments with the object of extracting the iron by means of a solution of sodium copper chloride, such as is used for the determination of carbon in iron and steel; this solution is prepared from copper sulphate and sodium chloride as previously described by one of us (*Chem. News*, **52**, 16). The determination is rendered difficult by the fact that the precipitated copper produced in the first instance is only very slowly soluble in the cold neutral solution; but on heating the liquid, or allowing it to stand, a copious, basic iron precipitate is obtained, while the addition of even diluted acids causes partial decomposition of the slag. We have tried the use of neutral and acid citrates and tartrates to prevent this precipitation, but with little success.

We have, however, met with considerable success by adding about 50 c.c. of the solution to a gram of the finely-divided sample, and allowing it to stand, with occasional stirring, for about half an hour in the cold. By this means a perfectly clear solution is obtained, and most of the iron passes into solution. The liquid is filtered, and the residue, after being washed by decantation, is treated with repeated small quantities of the cold solvent, and the precipitated copper is broken up and continually stirred with a glass rod until, ultimately, all is dissolved. The liquid is then filtered and the precipitate washed on to a small, ashless filter paper, dried, ignited, and weighed. The first filter paper we have always found retains too much copper and iron salts in the tissue to allow of its being used in the ordinary way, and any acid used for washing the paper would decompose the slag. The residue readily washes off, and is obtained in the form of small, black, or nearly black, particles, with all the appearance of slag.

The result of our examination of the four samples prepared for these experiments is as follows:—

	Best.		Common.	
	Bar.	Sheet.	Bar.	Sheet.
Slag per cent.	3·83	2·58	3·85	2·85
Loss	1·25 per cent.		1·00 per cent.	

We have not yet had sufficient experience with the method to speak definitely of its accuracy as compared with Eggertz's iodine method or other processes. We have, however, subjected two samples of tap cinder to the same treatment and found them to be apparently unattacked by the solvent, and to increase in weight ultimately by 5·69 and 5·66 per cent. respectively. This increase of weight is due to oxidation of the ferrous compound during the ignition of the residue. The above results are, therefore, slightly too high, and if the method were regularly used, a deduction of about 5 per cent. for oxidation might be made, or the determination carried out on a weighed filter. We may add that the slag obtained from the samples of wrought iron exactly resembled the residue obtained from tap cinder; and this, together with the character of the results themselves, leads us to consider them approximately correct. It will also be observed that the results of the determinations by the chlorine process, though all necessarily low, as previously explained, are in the same order as those obtained by the copper sodium chloride solution.

The experiments appear to us to prove that the actual weight of slag in best and common iron is, for practical purposes, identical, and that the difference in yield in the puddling furnace and on reheating is not due to variations in the total weight of slag in the puddled bar or finished irons.

The amount of total phosphorus retained by the crude iron appears to have a more direct influence on the loss in reheating than the proportion of slag, and we are inclined to believe that more information is obtained by the ordinary analysis of the samples than by the separate determination of the slag.

LII.—*Studies on Isomeric Change.* No. IV. *Halogen Derivatives of Quinone.* Part I.

By Arthur R. Ling.

The following work, an account of which I have now the honour of presenting to the Chemical Society, had for its primary object the study of isomeric change, in extension of my previously-published observations on this phenomenon (Trans., 1887, **51**, 147 and 782; 1889, **55**, 583). During its progress, however, I have had occasion to examine all the known chloro-, bromo-, and chlorobromo-derivatives of quinone, and I can, for the most part, confirm the observations of other chemists as to their properties; in cases where this is not so, or in which I have improved the methods of preparing these derivatives, I have given my experiments in detail. Several new halogen derivatives of quinone will be described.

Paradichloroquinone.—This compound was prepared as described by Hantzsch and Schniter (*Ber.*, **20**, 2279) by treating quinone twice with concentrated (fuming) hydrochloric acid, and oxidising after each treatment. It may also be prepared by the following method, which, if it does not give quite as large a yield, has the advantage of being much more rapid:—Finely-pulverised quinol (50 grams) is suspended in concentrated hydrochloric acid (250 c.c.), specially prepared by saturating the ordinary concentrated acid with hydrogen chloride at 0°, and coarsely-pulverised potassium chlorate (37 grams, equivalent to 2 mols. of chlorine) is gradually added. Experiment has proved that the product is the same, whether the addition of the chlorate extends over one hour or eight hours; the temperature is kept at about 80°. The product is placed aside for about 12 hours, at the end of which time it has the appearance of a semi-solid, pulpy mass of crystals. The liquid portion is then drained off by means of the air-pump, and the crystals washed with cold water to remove potassium chloride, &c.; the paradichloroquinol which remains is almost pure, and, after crystallisation from boiling water, melts constantly at 172°. To obtain the quinone, the crude, moist quinol is suspended in dilute sulphuric acid, oxidised carefully with potassium dichromate, the product washed with water, dried, and finally washed with ether, when almost pure paradichloroquinone, weighing 25—30 grams and melting at 158—160°, remains; after crystallisation from alcohol, it melts at 161°. Analysis:—

0·3039 gram of substance gave 0·4941 gram AgCl.

	Calculated. $C_6H_2Cl_2O_2$.	Found.
Cl	40·11 per cent.	40·20 per cent.

The aqueous mother liquor and washings from the crude quinol contain, besides potassium chloride, monochloroquinol, which was identified by its melting point and that of the quinone obtained by oxidising it, and by analysis. Other compounds are present, and as a considerable amount of this bye-product has been collected from numerous experiments, I intend to make a complete examination of it.

Metadichloroquinone.—This compound is obtained in small quantity by adding trichlorophenol to nitric acid (sp. gr. 1·5), cooled in a freezing mixture of ice and salt, but the yield is augmented by the following modification:—Trichlorophenol (25 grams) is dissolved in alcohol (100 c.c.), the solution cooled in a freezing mixture of ice and salt, and nitric acid (sp. gr. 1·5) (50 grams), also cooled, gradually dropped in, the alcoholic solution being kept in agitation meanwhile; after about two hours, metadichloroquinone separates in yellow needles, and when crystallised from alcohol, weighs at most 10 grams, and melts at 121°. The alcoholic filtrate, when carefully added to water, yields a red, varnish-like substance, which becomes semi-solid after a time, and is free from nitrophenol, but attempts to isolate pure substances from it have hitherto been unsuccessful. The best method of preparing metadichloroquinone is that devised by Kehrmann and Tiesler (*J. pr. Chem.* [2], **40**, 480) by the action of chromic acid on trichlorophenol dissolved in glacial acetic acid. The product obtained by this method is free from resinous substances, but is not exclusively metadichloroquinone, as stated by Kehrmann and Tiesler; in the crude state it consists of yellow, microscopic needles, and melts at 115—120°. This is suspended in water (10 parts) at 70°, and after passing a current of sulphurous anhydride through the mixture for 10 minutes, the solution is filtered from the undissolved, black, nodular particles (see below), and the filtrate allowed to remain; metadichloroquinol separates after a while in colourless needles, of melting point 159—160°, and a further quantity may be obtained by evaporating the filtrate. After purification, metadichloroquinol melts at 164°, as stated by Kehrmann and Tiesler (*loc. cit.*). The above-mentioned black, nodular particles, when allowed to remain in contact with alcohol, break up, and the dark, superficial coating dissolves, leaving a yellow substance which melts at 117—120°; the latter, after being crystallised repeatedly from light petroleum, melts at about 125°, and has the form of small, yellow, feathery, felted needles, quite distinct from metadichloroquinone; it is now under investigation.

Diacetylmetadichloroquinone.—This compound has been described by Levy (*Ber.*, **16**, 1445), who records the melting point as 66·5°; more recently, however, Kehrmann and Tiesler (*loc. cit.*) give 98° as the melting point. Metadichloroquinol dissolves in acetic anhydride with the evolution of heat, but only a small amount of the diacetyl derivative is formed. The whole of the quinol is converted into diacetyl derivative, however, when it is boiled in a reflux apparatus with acetic anhydride for about an hour. The product is extremely difficult to purify, and even after repeatedly evaporating with alcohol, it usually still contains acetic anhydride. A specimen, after crystallisation from dilute alcohol, was obtained in delicate needles and prisms, and melted at 76°. Analysis:—

0·145 gram of the substance gave 0·1604 gram AgCl.

	Calculated. $C_{10}H_8Cl_2O_4$.	Found.
Cl	26·99 per cent.	27·45 per cent.

I have since prepared another specimen which behaved as follows:—When the temperature was very slowly raised, it melted even as high as 111—113°, and resolidified at about 66° (Levy's temperature); whilst, if the temperature was quickly raised, it melted at 85—86°.

Metadichloroquinone is also obtained in small quantity by dropping diorthochloroparabromophenol into cooled nitric acid (see below). As the last-mentioned compound has not as yet been described, I will here give its method of preparation and characteristics.

Diorthochloroparabromophenol.—Sulphuryl chloride (40 grams) is added to fused parabromophenol (25 grams); the product is freed from acid, dissolved in sodium hydroxide solution, and reprecipitated with acid. After repeated crystallisation from dilute alcohol, it is obtained in silky needles, melts at 65°, and possesses a faint but penetrating odour. When recrystallised from light petroleum, it forms magnificent, long, silky needles, and melts constantly at 66·5°. Analysis:—

0·3116 gram of substance gave 0·6171 gram of mixed chloride and bromide of silver.

	Calculated. $C_6H_2Cl_2Br{\cdot}OH$.	Found.
Cl Br	62·39 per cent.	62·93 per cent.

When the dichlorobromophenol is dissolved in glacial acetic acid, and the solution heated with a slight excess of nitric acid (sp. gr. 1·42), it yields dichloroparanitrophenol (m. p. 125°) and orthochlororthoparadinitrophenol (m. p. 110—111°). Analyses of the potassium salts:—

I. 0·2243 gram of substance lost 0·0156 gram at 120°, and gave 0·0754 gram K_2SO_4.

	Calculated. $C_6H_2Cl_2(NO_2)\cdot OK + H_2O$.	Found.
H_2O	6·81 per cent.	6·95 per cent.
K	14·77 „	15·06 „

II. 0·2786 gram of substance lost 0·017 gram at 120°, and gave 0·0916 gram K_2SO_4.

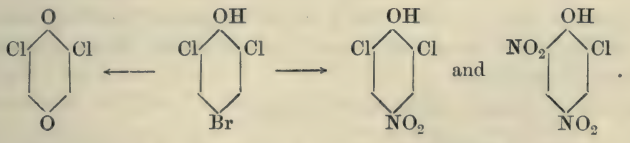
	Calculated. $C_6H_2Cl(NO_2)_2\cdot OK + H_2O$.	Found.
H_2O	6·55 per cent.	6·10 per cent.
K	14·20 „	14·73 „

When the dichlorobromophenol (16 grams) is added to nitric acid (sp. gr. 1·5; about 70 grams) cooled in a freezing mixture of ice and salt, it yields a small quantity of metadichloroquinone; it is purified by crystallisation from alcohol, and melts at 121°, giving a quinol melting at 164°. Analysis:—

0·1671 gram of substance gave 0·2684 gram AgCl.

	Calculated. $C_6H_2Cl_2O_2$.	Found.
Cl	40·11 per cent.	39·73 per cent.

The above facts therefore establish the constitution of the dichlorobromophenol, thus:—



Metadibromoquinone.—This is obtained in small quantity, as stated by Levy and Schultz (*Annalen*, **210**, 158), by adding ordinary tribromophenol to cold nitric acid (sp. gr. 1·5). When pure, it forms golden-yellow leaflets, and melts at 131° (compare Heinichen, *Annalen*, **253**, 253). It is obtained in good yield by oxidising dibromoparamidophenol sulphate with a faintly acid solution of potassium chromate. The paramidophenol sulphate crystallises from dilute sulphuric acid in greyish needles. Analysis:—

I. 0·3557 gram of substance lost 0·0369 gram at 130°, and gave 0·122 gram $BaSO_4$.

II. 0·4296 gram of substance gave 0·1443 gram $BaSO_4$.

	Calculated. $[C_6H_2Br_2(NH_2)\cdot OH]_2,H_2SO_4 + 4H_2O$.	Found. I.	II.	
H_2O	10·22 per cent.	10·37	—	per cent.
H_2SO_4 ..	13·92 ,,	14·42	14·16	,,

Metadibromoquinol is obtained by reducing the quinone with sulphurous acid; it forms long, (almost?) colourless leaflets, and melts at 163—164°. Analysis:—

0·4296 gram of substance gave 0·5984 gram AgBr.

	Calculated. $C_6H_2Br_2(OH)_2$.	Found.
Br	59·70 per cent.	59·26 per cent.

Metadibromoquinol is sparingly soluble in cold water or benzene, readily in the boiling liquids, and still more so in alcohol and glacial acetic acid; on oxidation, the quinone melting at 131° is obtained:—

Metachlorobromoquinone.—This compound is obtained in small yield when orthochlororthoparadibromophenol (m. p. 76°); Garzino (*Atti. Real. Accad. Torino*, **25**; also *Ber.* **25**, Ref. 120), is added to nitric acid (sp. gr. 1·5) cooled by ice and salt. It crystallises from alcohol in yellow needles resembling metadichloroquinone, and melts at 114—115°. Nef (*Amer. Chem. J.*, **13**, 422) has recently prepared this compound and established its constitution. He states that it melts at 113°. 75 grams of orthochlororthoparadibromophenol give 6 grams of pure metachlorobromoquinone; the remainder of the product being varnish-like substances, from which chlorobromoparanitrophenol (m. p. 137°; see Trans., 1889, 57) and orthochlororthoparadinitrophenol (m. p. 110—111°) were obtained, and identified by their melting points as well as by analyses of their barium and potassium derivatives.

Analysis of metachlorobromoquinone:—

0·2596 gram of substance gave 0·3876 gram of mixed chloride and bromide of silver.

	Calculated. $C_6H_2ClBrO_2$.	Found.
$\left.\begin{matrix}Cl\\Br\end{matrix}\right\}$	52·14 per cent.	52·00 per cent.

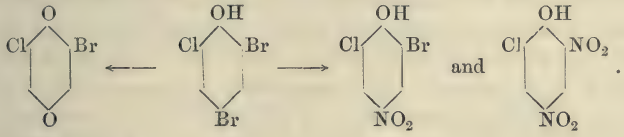
Metachlorobromoquinol is prepared by reducing the quinone with sulphurous acid; it resembles, in form and solubility, the corresponding dibromo-derivative, and melts at 154—155°. The following result was obtained on analysis:—

0·3362 gram of substance gave 0·4957 gram of mixed chloride and bromide of silver.

	Calculated. $C_6H_2ClBr(OH)_2$.	Found.
Cl Br }	51·67 per cent.	51·36 per cent.

The last-described quinol yields metachlorobromoquinone, melting at 114—115°, on oxidation. *Diacetylmetachlorobromoquinol* was not obtained in the pure state, as the same difficulties were encountered as mentioned above under the corresponding dichloro-derivative; it, however, appears to melt below 100°.

The relation of Garzino's chlorodibromophenol to metachlorobromoquinone and to the above-mentioned nitrophenol derivatives is shown by the following symbols:—



Paradichlorobromoquinone.

In a note read before the Chemical Society, March 6, 1890 (Proc., 1890, 32), I stated that when paradichloroquinone is brominated, paradichlorobromoquinone is obtained together with an isomeride, and I was led to this conclusion by certain observations made by Hantzsch which I have since proved to be incorrect. The product which I obtained apparently contained a small amount of chlorodibromoquinone, due to the presence of monochloroquinone in the crude paradichloroquinone employed (see above under paradichloroquinone). I separated pure paradichlorobromoquinone from this product, and the remaining portion which I believed to be an isomeride appears to have been a mixture of dichlorobromo- and chlorodibromo-quinone, together with a small quantity of tetra-halogen derivative; this view is supported by the fact that the bromine determinations made with the supposed isomeric dichlorobromoquinone were too high. The presence of tetra-halogen derivative is accounted for as follows:—When the tri-halogen derivatives of quinone are repeatedly recrystallised from alcohol, they undergo partial decomposition, the solution becoming strongly acid. When an alcoholic solution of either of the halogen derivatives of quinone is evaporated, the residue consists almost entirely of resinous substances. It is thus probable that halogen is split off, and a certain amount of tetra-halogen derivative produced every time the tri-halogen derivatives are crystallised from alcohol. This tetra-halogen quinone is very much more stable, and at the same time much less soluble in alcohol, than the tri-derivatives, and is therefore increased relatively in quantity each time the tri-derivatives are recrystallised from this solvent.

Paradichlorobromoquinone is obtained in good yield when para-dichloroquinone is dissolved in glacial acetic acid, and bromine (1 mol. proportion) dropped into the solution. When the bromination is complete, which is usually the case after some hours, the solution is poured into water, the compound collected, washed, suspended in water (about 10 parts), and a current of sulphurous anhydride passed through at the ordinary temperature; it is then filtered from any unattacked tetra-halogen quinone which may be present (compare Graebe, *Annalen*, **263**, 16). The sulphurous anhydride is expelled from the filtrate by boiling, and after cooling and rendering acid with dilute sulphuric acid, an excess of potassium dichromate solution is cautiously added with agitation, and the precipitated paradichlorobromoquinone collected, washed, dried, and crystallised from alcohol. It forms thin, lustrous, yellow plates, resembling trichloroquinone, melts at 160—161°, and is readily soluble in boiling alcohol, but only sparingly in the cold; readily soluble in glacial acetic acid, benzene, and chloroform, but somewhat sparingly in boiling light petroleum. The following results were obtained on analysis:—

I. 0·2329 gram of substance gave 0·4217 gram of mixed chloride and bromide of silver.

II. 0·2198 gram of substance gave 0·4039 gram of mixed chloride and bromide of silver.

	Calculated. $C_6HCl_2BrO_2$.	Found. I.	Found. II.
Cl, Br ……	58·98 per cent.	57·54	58·37 per cent.

When paradichlorobromoquinone is heated with aqueous alkali, chloranilic acid is produced. The following result was obtained on analysing a specimen of air-dried chloranilic acid derived from the last-mentioned quinone:—

*0·0794 gram of substance gave 0·1026 gram AgCl.

	Calculated. $C_6Cl_2(OH)_2O_2 + H_2O$.	Found.
Cl ………	31·27 per cent.	31·95 per cent.

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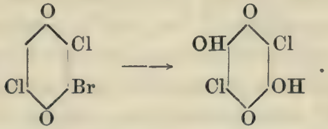
* The above result was obtained with an exceedingly small weight of substance, a larger quantity not being available. The conclusion, as to the constitution of the dichlorobromoquinone, drawn from it, will, however, be found to be confirmed in a subsequent portion of the paper (see under paradichlorodibromoquinone). The chloranilic acid was characterised by its potassium salt.

This result establishes, therefore, the constitution of the dichlorobromoquinone, thus:—



Pardichlorobromoquinol is obtained by reducing the quinone with sulphurous acid. It separates from its aqueous solution in small, lustrous prismatic needles containing 1 mol. H_2O, melts at 124—126° when the temperature is raised slowly, partially resolidifies above this, and again melts at 134—135°. It loses its water of crystallisation at 70°, as the following determination shows:—

0·3552 gram of substance lost 0·0232 gram at 70°.

	Calculated. $C_6HCl_2Br(OH)_2 + H_2O$.	Found.
H_2O	6·52 per cent.	6·53 per cent.

The anhydrous compound crystallises from chloroform in small, felted needles, and melts at 133·5°; it is readily soluble in boiling water, chloroform, and carbon bisulphide, sparingly in the cold liquids, and easily in alcohol.

The following results were obtained on analysis:—

I. 0·127 gram of substance gave 0·236 gram of mixed chloride and bromide of silver, and this lost 0·0216 gram on ignition in a current of dry chlorine.

II. 0·173 gram of substance gave 0·32 gram of mixed chloride and bromide of silver, and this lost 0·0305 gram on ignition in a current of dry chlorine.

	Calculated. $C_6HCl_2Br(OH)_2$.	Found. I.	Found. II.
Cl	27·51 per cent.	28·19	27·33 per cent.
Br	31·00 ,,	30·56	31·69 ,,

Diacetylparadichlorobromoquinol is prepared by boiling the quinol in a reflux apparatus for about an hour with acetic anhydride. It crystallises from boiling light petroleum in silky needles, and melts at 158—159°. Analysis:—

0·1883 gram of substance gave 0·2611 gram of mixed chloride and bromide of silver.

	Calculated. $C_6HCl_2Br(OC_2H_3O)_2$.	Found.
Cl } Br }	44·15 per cent.	44·07 per cent.

Paradichlorobromoquinol is also obtained together with paradichlorodibromoquinol when finely pulverised paradichloroquinone is boiled with concentrated fuming hydrobromic acid. These products were analysed and characterised, but it is unnecessary to give details.

Metadichlorobromoquinone is prepared in a similar manner to the para-derivative by treating metadichloroquinone dissolved in glacial acetic acid with bromine (1 mol. proportion). After crystallisation from boiling alcohol or light petroleum, it is obtained in thin, lustrous, yellow plates. It resembles the para-derivative in general form and solubility, and melts at 168°. In my former note (Proc., *loc. cit.*), I stated that this compound has not a sharp melting point, and I gave the value 175—180°. This is, however, erroneous, and the cause of the misstatement is that the quinone formerly described had been crystallised repeatedly from alcohol, and was contaminated with tetra-halogen derivative (see above under paradichlorobromoquinone). The following result was obtained on analysing a specimen of metadichlorobromoquinone:—

0·2224 gram of substance gave 0·4083 gram of mixed chloride and bromide of silver; this lost 0·0388 gram on ignition in a current of dry chlorine.

	Calculated. $C_6HCl_2BrO_2$.	Found.
Cl........	27·73 per cent.	27·17 per cent.
Br	31·25 ,,	31·33 ,,

When metadichlorobromoquinone is heated with dilute alkali, chlorobromanilic acid is obtained. The potassium salt was analysed with the following result:—*

0·1332 gram of substance lost 0·0134 gram at 130°, and gave 0·0632 gram K_2SO_4.

	Calculated. $C_6ClBr(OK)_2O_2 + 2H_2O$.	Found.
H_2O......	9·84 per cent.	10·06 per cent.
K........	21·34 ,,	21·24 ,,

The constitution of metadichlorobromoquinone is therefore established by this result, thus:—

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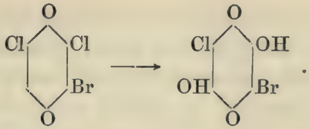
[*] A halogen determination was also made on the sodium salt.

	Calculated. $C_6ClBr(ONa)_2O_2 + 4H_2O$.	Found.
Cl............	9·60 per cent.	9·45 per cent.
Br...........	21·65 ,,	20·13 ,,



Metadichlorobromoquinol is obtained by reducing the quinone with sulphurous acid; it is also formed together with paradichlorodibromoquinone (see below), when metadichloroquinone is boiled with concentrated fuming hydrobromic acid. It is, however, best prepared as follows:—Finely-pulverised metadichloroquinol (1 mol.) is suspended in dry carbon bisulphide or chloroform* (20 parts), and bromine (1 mol.) dropped in with agitation. After remaining for some hours with constant shaking, the liquid portion is removed, and the crude quinol spread upon a porous tile until the greater portion of the hydrogen bromide has passed off. It is generally pure after one crystallisation from boiling water or chloroform; it separates from either solvent in bunches of anhydrous, colourless needles, melts at 135°, and resembles the para-derivative as regards solubility. Analysis:—

0·1554 gram of substance gave 0·2842 gram of mixed chloride and bromide of silver, and this lost 0·0266 gram on ignition in a current of dry chlorine.

	Calculated. $C_6HCl_2Br(OH)_2$.	Found.
Cl	27·52 per cent.	27·28 per cent.
Br........	31·00 ,,	30·75 ,,

Diacetylmetadichlorobromoquinone is prepared by boiling the quinol in a reflux apparatus with acetic anhydride. It crystallises from boiling benzene in colourless, microscopic needles, melts at 173—174°, and is readily soluble in chloroform, sparingly in cold alcohol and benzene, readily in the hot liquids; it is only sparingly soluble in boiling light petroleum, and almost insoluble in cold. Analysis gave the following result:—

0·2684 gram of substance gave 0·3681 gram of mixed chloride and bromide of silver, and this lost 0·0353 gram on ignition in a current of dry chlorine.

	Calculated. $C_6HCl_2Br(O{\cdot}C_2H_3O)_2$.	Found.
Cl	20·76 per cent.	20·19 per cent.
Br........	23·39 ,,	23·61 ,,

---

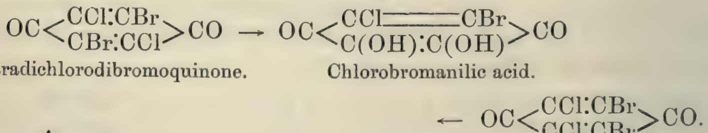
* When either of the dichloroquinols is treated with bromine in glacial acetic acid solution, oxidation accompanies bromination, and the quinone derivatives are obtained.

Tetrachloroquinone (chloranil) is conveniently prepared by passing a current of chlorine through the crude product of the action of potassium chlorate and hydrochloric acid on quinol (paradichloroquinol; see above) dissolved in glacial acetic acid, until it consists of a magma of yellow scales. The product is a mixture of tri- and tetra-chloroquinone, similar to that obtained from phenolsulphonic acid by Knapp and Schultz's method (*Annalen*, **210**, 175), and these are separated according to Graebe's latest directions (*Annalen*, **263**, 16), and crystallised from toluene. Pure tetrachloroquinone melts at 290°, as stated by Graebe (*loc. cit.*).

Tetrabromoquinone (bromanil) is obtained in almost theoretical yield when quinol (30 grams; 1 mol.) is dissolved in glacial acetic acid (300 c.c.), and bromine (4 mols.) run in with agitation. After adding all the bromine, the mixture is allowed to remain for some hours, a small quantity of nitric acid is then added, and it is heated on the water-bath for a short time to complete the bromination and oxidise any quinol derivative which may be present. When cool, it is poured into water, and the precipitated tetrabromoquinone collected, washed, dried, and crystallised from glacial acetic acid, and subsequently from benzene. The pure compound melts at 300°, as stated by Graebe and Welltner (*Annalen*, **263**, 31).

The remainder of my experiments deal with paradichlorodibromo- and metadichlorodibromo-quinone and their derivatives, and before describing them, it will be necessary to make some introductory remarks.

S. Levy stated (*Ber.*, **18**, 2366) that the so-called anilic acids were orthodihydroxy-derivatives of quinone, since he found that the same dihydroxychlorobromoquinone (chlorobromanilic acid) is obtained from both paradichlorodibromo- and metadichlorodibromo-quinone* on treating them with alkali; for example:—



$$\mathrm{OC}<\begin{matrix}\mathrm{CCl{:}CBr}\\ \mathrm{CBr{:}CCl}\end{matrix}>\mathrm{CO} \rightarrow \mathrm{OC}<\begin{matrix}\mathrm{CCl{=\!=}CBr}\\ \mathrm{C(OH){:}C(OH)}\end{matrix}>\mathrm{CO} \leftarrow \mathrm{OC}<\begin{matrix}\mathrm{CCl{:}CBr}\\ \mathrm{CCl{:}CBr}\end{matrix}>\mathrm{CO}.$$

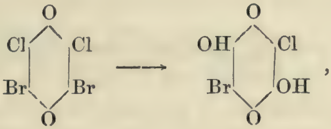
Paradichlorodibromoquinone. Chlorobromanilic acid.

Metadichlorodibromoquinone.

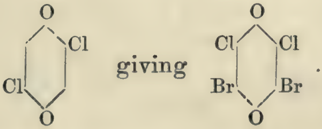
---

[*] Levy (*loc. cit.*) publishes crystallographic measurements of paradichlorodibromoquinone, and the corresponding quinol, made for him by T. Liweh (see also *Zeits. Kryst. Min.*, **11**, 246), and these indicate that the quinone is not isomorphous with metadichlorodibromoquinone (see Levy, *Ber.*, **16**, 1444), but that the two quinols are isomorphous. Mr. W. J. Pope has, however (see p. 573), recalculated Liweh's results, and found from his conclusion that paradichlorodibromoquinone is not isomorphous with the so-called metadichlorodibromoquinone is unsupported by the data.

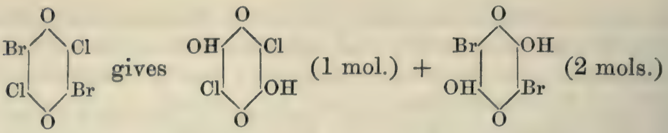
It was, however, subsequently proved by Hantzsch (*Ber.*, **19**, 2398) and by Nietzki (*ibid.*, 2727) that nitranilic acid, which is the analogue of chloranilic and bromanilic acids, is a paradihydroxy-derivative, thus, $CO<\begin{matrix}C(NO_2):C(OH)\\C(OH):C(NO_2)\end{matrix}>CO$; and, finally, Hantzsch found (*Ber.*, **20**, 1303) that paradihydroxydibromoquinone, which he obtained by treating the basic sodium salt of paradihydroxyquinonedicarboxylic acid with bromine-water, is identical with bromanilic acid. It therefore became necessary to reconcile this result with those of Levy. Accordingly, Hantzsch and Schniter (*Ber.*, **20**, 2279) re-examined the two dichlorodibromoquinones from para- and meta-dichloroquinone, and also the corresponding quinols and their diacetyl derivatives, and finally arrived at the conclusion that the two sets of compounds from both sources were identical each to each. Inasmuch, therefore, as the dichlordibromoquinone prepared from both para- and metadichloro-quinone yielded, on treatment with alkali, chlorobromanilic acid, Hantzsch and Schniter concluded that it was metadichlorodibromoquinone,



and that an isomeric change occurs when paradichloroquinone is brominated,

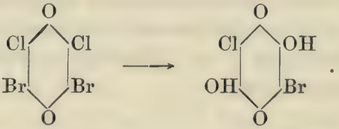


Previous to the appearance of Hantzsch and Schniter's paper, I had arrived at an identical conclusion, but withheld my views in order to investigate the subject more fully. This I have since done, and my experiments prove that the dichlorodibromoquinone obtained on brominating paradichloroquinone, at the ordinary temperature, and at the boiling point of glacial acetic acid, is a homogeneous compound, but that it does not give chlorobromanilic acid on treatment with alkali, as stated by Levy, and by Hantzsch and Schniter, but a molecular compound consisting of chloranilic acid (1 mol.) and bromanilic acid (2 mols.). There is, therefore, no reason for regarding this dichlorodibromoquinone as anything but the normal product, which will readily be seen on comparing the symbols:—

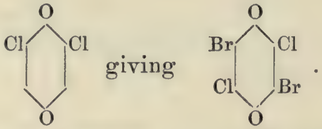


Paradichlorodibromoquinone. Chloranilic acid. Bromanilic acid.

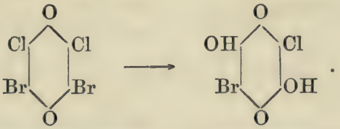
On studying the bromination of metadichloroquinone, I was surprised to find that the dichlorodibromoquinone obtained by brominating this at a high temperature also gave the same compound, consisting of chloranilic acid (1 mol.) and bromanilic acid (2 mols.) on treatment with alkali. Obviously, therefore, this could not be the normal product, metadichlorobromoquinone, which would give only chlorobromanilic acid, thus:—



I can, therefore, confirm Hantzsch and Schniter's statement that the compound and its derivatives obtained by brominating paradichloroquinone are identical in all respects with those obtained by brominating metadichloroquinone when the experiments are conducted at a high temperature. An isomeric change must, however, be assumed to occur when metadichloroquinone is brominated under these circumstances,

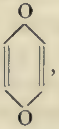


An extended study of the bromination products of metadichloroquinone at high and low temperatures, and that of metadichloroquinol, has completely confirmed this view, and my remaining results may thus be summed up:—When metadichloroquinone is brominated in glacial acetic acid solution at a temperature of 15—20°, a mixture consisting for the most part of the normal product, metadichlorodibromoquinone, together with a smaller quantity of paradichlorodibromoquinone, is obtained; whilst, if the reaction is performed at the boiling point of glacial acetic acid, paradichlorodibromoquinone is exclusively formed. Furthermore, when metadichlorobromoquinol (m. p. 135°) is suspended in an anhydrous menstruum and brominated, the normal product is produced, and this gives metadichlorodibromoquinone on oxidation; the latter then yields chlorobromanilic acid on treatment with alkali, thus:—

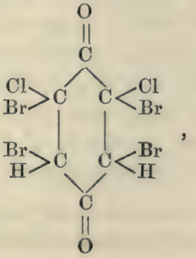

Metadichlorodibromo-quinone. Chlorobromanilic acid.

Mr. W. J. Pope, who has kindly furnished me with crystallographic measurements of several of the compounds described in this paper, finds that the last-mentioned dichlorodibromoquinone is crystallographically distinct from the isomeric para-derivative. The two compounds melt, however, within a degree of one another, and the melting points of their derivatives are very close; this is, however, not so surprising when it is remembered that all the tetra-halogen quinones and their derivatives are very close to one another in melting point. Mr. Pope also finds that paradichlorodibromoquinone, prepared from the two sources, gives measurements which are identical within the limits of experimental error.

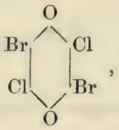
Representing quinone by Fittig's formula,



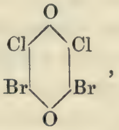
it cannot be strictly regarded as a benzene derivative, and an intramolecular redistribution of affinities must occur when it is reduced to quinol, a true benzene derivative. Nef has recently pointed out (*J. pr. Chem.* [2], **42**, 161) that quinone unites with 4 atoms of halogen to form derivatives of diketohexamethylene, and it thus appears probable that, whenever quinone is treated with halogen, the formation of an additive compound precedes that of a substitution derivative. It is conceivable, therefore, that when metadichloroquinone is treated with 2 mol. proportions of bromine, the dichloridetetrabromide (dichlorotetrabromoparadiketohexamethylene),



is the primary product, and that this subsequently decomposes at a high temperature (that of boiling glacial acetic acid) into paradichlorodibromoquinone,



whilst, at the ordinary temperature, it decomposes for the most part into metadichlorodibromoquinone,



The production of paradichlorodibromoquinone requires the assumption of an intramolecular change, but such a change must also be assumed when quinone is converted into quinol. That such an intramolecular change would be likely to occur is, however, borne out by Nef's observation (*loc. cit.*) that quinone tetrabromide, on boiling with aqueous alcohol, yields a mixture of para- and meta-dibromoquinone. Before passing to the experimental portion, I will again draw attention to the fact that metadichloroquinol, when brominated at a temperature at which the corresponding quinone yields exclusively paradichlorodibromoquinone, gives the normal product. This is probably because the quinol is a true benzene derivative, and, therefore, as a saturated compound, direct substitution takes place.

Bromination of Paradichloroquinone.

Paradichlorodibromoquinone.—As already mentioned, Hantzsch and Schniter (*loc. cit.*) have put forward the view that when paradichloroquinone is brominated, metadichlorodibromoquinone is produced. This observation led me to study the bromination products of paradichloroquinone,* paradichloroquinol, and its diacetyl derivative, under various conditions, both at high and low temperatures; these experiments were made on an extensive scale, and the derivatives obtained were fractionally crystallised from every available solvent, the result being that they were found in all cases to be homogeneous substances and the normal products of the reactions. Several experiments were also made to determine the nature of the chlorination product of paradibromoquinone; in this case bromine is partially replaced by chlorine, and the products are probably chloranil, chlorotribromoquinone, and a dichlorodibromoquinone which was isolated and proved to be the para-derivative.

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* It may be added that the bromination of paradichloroquinone with both concentrated hydrobromic acid and bromine has been studied.

Paradichlorodibromoquinone is best prepared by dissolving paradichloroquinone (1 mol.) in glacial acetic acid (10 parts) at 70—80°, and dropping bromine (2 mols.) into the hot solution. After adding all the bromine, the crystalline magma is allowed to remain for a while, and then poured into an excess of water, collected, and washed. It is then suspended in water, and treated with potassium dichromate and dilute sulphuric acid, the object of this being to oxidise the tetra-halogen quinol which is invariably produced in small quantity; after this, it is again collected, washed, and dried; the yield is practically quantitative. It is crystallised first from glacial acetic acid, and subsequently from benzene. It forms six-sided plates, melts at 292°, and is sparingly soluble in glacial acetic acid at the ordinary temperature, more readily in the boiling liquid, and easily in boiling benzene; it is almost insoluble in cold alcohol, and only very slightly soluble in boiling. On adding light petroleum to its solution in benzene, it slowly separates out. The following result was obtained on analysing this compound:—

0·3824 gram of substance gave 0·7587 gram of mixed chloride and bromide of silver, and this lost 0·1004 gram on ignition in a current of dry chlorine.

	Calculated. $C_6Cl_2Br_2O_2$.	Found.
Cl......	21·19 per cent.	21·63 per cent.
Br......	47·76 „	47·19 „

Mr. W. J. Pope has measured some crystals of the above compound, and finds them to be identical in form with those of the so-called metadichlorodibromoquinone (Levy, *Ber.*, **16**, 1444); whereas, Liweh (*Zeit. Kryst. Min.* **11**, 247), as before stated, shows that the two compounds have different axial relations. Mr. Pope has, however, gone over Liweh's calculations and reports as follows:—"In this paper (*loc. cit.*), Liweh states that a comparison of the crystallographic elements of paradichlorodibromoquinone, $a : b : c = 1·446 : 1 : 2·850$; $\beta = 77° 30'$ with those of metadichlorodibromoquinone, $a : b : c = 1·445 : 1 : 3·0286$; $\beta = 74° 31'$ (Levy, *loc. cit.*), shows that these two compounds are not isomorphous, the ratio $a : b$ only remaining unaltered in the two substances, whilst the axis c is altered." "It can, however, be readily shown by readjusting the symbols allotted to the crystals of these two substances that the axial relations are practically the same in both." "Thus, starting from the para-compound $a : b : c$

$= 1·446 : 1 : 2·850$; $\beta = 77° 30'$, by altering the symbols of the various forms, the axial relations $a : b : c = 1·4460 : 1 : 2·9025$; $\beta = 73° 25'$ can be obtained, a set of values which are in fairly close agreement with those given by Liweh to the so-called metadichlorodibromoquinone." "The difference in the axial relations observed by Levy and Liweh is therefore only apparent, and this is confirmed by my own measurements, according to which the substances in question are crystallographically identical." "Any support which the crystallographic observations of Levy and Liweh have previously afforded to the view that the quinones from both sources are distinct compounds is thus rendered valueless."

When paradichlorodibromoquinone is heated with aqueous potassium or sodium hydroxide solutions (4—10 per cent.), it yields a compound consisting of chloranilic acid (1 mol.) and bromanilic acid (2 mols.), which cannot be separated into its constituents by crystallisation of either of its salts.

The sodium salt crystallises from water in massive, dark, almost black prisms which are red by transmitted light, belonging to the anorthic system, $a : b : c = 0·8825 : 1 : 0·8163$; $\alpha = 69° 48'$; $\beta = 87° 14'$; $\gamma = 72° 11'$. Analysis:—

I. 0·2224 gram of substance lost 0·0422 gram at 150°, and gave 0·0816 gram Na_2SO_4.

II. 0·2147 gram of substance lost 0·0403 gram at 150°, and gave 0·0779 gram Na_2SO_4.

III. 0·3171 gram of substance gave 0·2840 gram of mixed chloride and bromide of silver, and this lost 0·0489 gram on ignition in a current of dry chlorine.

	Calculated. $C_6Cl_2(ONa)_2O_2,2C_6Br_2(ONa)_2O_2 + 12H_2O$.	Found. I.	 II.	 III.	
H_2O......	18·65 per cent.	18·97	18·77	—	per cent.
Na.......	11·98 ,,	11·86	11·73	—	,,
Cl.......	6·15 ,,	—	—	6·04	,,
Br.......	27·75 ,,	—	—	27·71	,,

The potassium salt crystallises in slender, dark-red needles. Analysis:—

I. 0·2143 gram of substance lost 0·0205 gram at 150°, and gave 0·0959 gram K_2SO_4.

II. 0·1837 gram of substance lost 0·0169 gram at 150°, and gave 0·0825 gram K_2SO_4.

III. 0·2045 gram of substance gave 0·1855 gram of mixed chloride and bromide of silver, and this lost 0·0315 gram on ignition in a current of dry chlorine.

	Calculated. $C_6Cl_2(OK)_2O_2,2C_6Br_2(OK)_2O_2 + 6H_2O$.		Found. I.	II.	III.	
H_2O......	9·46	per cent.	9·56	9·20	—	per cent.
K........	20·50	,,	20·05	20·11	—	,,
Cl.......	6·22	,,	—	—	6·35	,,
Br.......	28·04	,,	—	—	27·68	,,

The dihydroxy-compound separates in brick-red scales on adding an excess of dilute hydrochloric acid to an aqueous solution of the alkali salts. The mean of two determinations obtained with a specimen of the substance dried at 120° gave the following values:—

	Calculated. $C_6Cl_2(OH)_2O_2,2C_6Br_2(OH)_2O_2$.	Found.
Cl.........	8·81 per cent.	8·08 per cent.
Br.......	39·75 ,,	40·64 ,,

To prove that the last-described substance was really a compound of chloranilic acid (1 mol.) and bromanilic acid (2 mols.), sodium chloranilate and bromanilate were dissolved in water in this proportion. The crystals obtained were measured by Mr. Pope, and found to have the same axial relations as those above given by him for the salt from paradichlorodibromoquinone, thus:—$a : b : c = 0·8825 : 1 : 0·8143$; $\alpha = 69° 56'$; $\beta = 87° 7'$; $\gamma = 72° 11'$. The axial relations of sodium chloranilate, bromanilate, and chlorobromanilate were also determined by Mr. Pope, thus:—Sodium chloranilate, $a : b : c = 0·8743 : 1 : ?$; $\alpha = 88° 8'$; $\beta = 89° 51'$; $\gamma = 72° 30'$. Sodium bromanilate, $a : b : c = 0·8768 : 1 : 0·8100$; $\alpha = 69° 28'$; $\beta = 87° 56'$; $\gamma = 71° 49'$. Sodium chlorobromanilate, $a : b : c = 0·888 : 1 : 0·814$; $\alpha = 69° 59'$; $\beta = 87° 3'$; $\gamma = 71° 58'$. A comparison of the elements of the two samples of the salt $C_6Cl_2(ONa)_2O_2,2C_6Br_2(ONa)_2O_2 + 12H_2O$, the one obtained from paradichlorodibromoquinone, and the other by mixing the constituents in the requisite proportions shows them to be crystallographically identical." "The differences between the axial relations of the various salts are small, but sufficiently great to characterise them as distinct compounds" (see also next paper). Analysis of the salt prepared by mixing sodium chloranilate (1 mol.) with sodium bromanilate (2 mols.), and crystallising the mixture from water:—

0·2921 gram of substance lost 0·0544 gram at 150°, and gave 0·1067 gram Na_2SO_4.

	Calculated. $C_6Cl_2(ONa)_2O_2,2C_6Br_2(ONa)_2O_2 + 12H_2O$.	Found.
H_2O..........	18·65 per cent.	18·62 per cent.
Na	11·98 ,,	11·83 ,,

The dihydroxy-derivative obtained by decomposing the last sodium salt with acid gave, on analysis:—Cl, 7·44 per cent.; Br, 41·32 per cent. Calculated:—Cl, 8·81 per cent.; Br, 39·75 per cent.

When paradichlorodibromoquinol is reduced by Graebe's method (see *Annalen*, **263**, 16) with hydriodic acid and phosphorus, the corresponding quinol is obtained, crystallising from benzene in flat needles, and melting at 235—236°; it gives a diacetyl derivative, which crystallises from benzene or glacial acetic acid in needles, and melts at 269—270°; compare Hantzsch and Schniter (*loc. cit.*).

Bromination of Metadichloroquinone (high temp.).

Paradichlorodibromoquinone is also formed by brominating metadichloroquinone in boiling glacial acetic acid solution. The same quantity of glacial acetic acid is employed as given above for the bromination of the paradichloroquinone, and the experiment is conducted in the same manner as the latter, only at the boiling point of the solution. The dichlorodibromoquinone obtained in this way is in every respect identical with that obtained from paradichloroquinone, thus: it melts at 292°, yields a quinol melting at 235—236°, which gives a diacetyl derivative melting at 269—270°; and further, Mr. Pope has established the identity of the two compounds by crystallographic measurement (see above). The following result was obtained on analysing the quinone:—

0·2062 gram of substance gave 0·4023 gram of mixed chloride and bromide of silver, and this lost 0·0538 gram on ignition in a current of dry chlorine.

	Calculated. $C_6Cl_2Br_2O_2$.	Found.
Cl	21·19 per cent.	21·01 per cent.
Br	47·76 ,,	46·84 ,,

This quinone gives the compound of chloranilic acid (1 mol.) and bromanilic acid (2 mols.) on treatment with alkali.

Analysis of the sodium salt:—

I. 0·3102 gram of substance lost 0·0568 gram at 150°, and gave 0·1144 gram Na_2SO_4.

II. 0·2109 gram of substance lost 0·0386 gram at 150°, and gave 0·0775 gram Na_2SO_4.

III. 0·5472 gram of substance gave 0·4899 gram of mixed chloride and bromide of silver, and this lost 0·0829 gram on ignition in a current of dry chlorine.

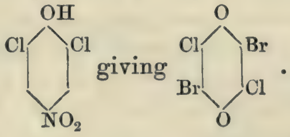
	Calculated. $C_6Cl_2(ONa)_2O_2,2C_6Br_2(ONa)_2O_2$ + $12H_2O$.	Found. I.	II.	III.	
H_2O......	18·65 per cent.	18·31	18·30	—	per cent.
Na.......	11·98 „	11·94	11·90	—	„
Cl.......	6·15 „	—	—	6·31	„
Br.......	27·75 „	—	—	27·23	„

Potassium salt:—

0·226 gram of substance lost 0·0218 gram at 150°, and gave 0·1033 gram K_2SO_4.

	Calculated. $C_6Cl_2(OK)_2O_2,2C_6Br_2(OK)_2O_2$ + $6H_2O$.	Found.
H_2O.........	9·46 per cent.	9·64 per cent.
K..........	20·50 „	20·49 „

I have previously described a compound as metadichlorodibromoquinone (Trans., 1887, 786), obtained by the action of bromine on dichloroparanitrophenol. I have carefully re-examined this, and find that it does not give chlorobromanilic acid on treatment with alkali, as stated (*loc. cit.*), but the molecular compound of chloranilic and bromanilic acids. The following values were obtained on analysing the sodium salt:—H_2O = 18·41 per cent.; Na = 11·91 per cent.; Cl = 6·02 per cent.; Br = 28·13 per cent. In the formation of this dichlorodibromoquinone, which must be the para-derivative, an isomeric change must occur, as shown by the following symbols:—



A dichlorodibromoquinone has been obtained by Krause (*Ber.*, **12**, 47) by the action of bromine on dichloroquinonechlorimide. He shows that this quinone gives chlorobromanilic acid on treatment with alkali, and analyses of the potassium, sodium, and silver salts, as also of the acid itself, agreeing closely with the theoretical, are recorded; hence, the quinone must have been metadichlorodibromoquinone (compare above). Such a constitution is hardly conceivable, taking into account the source—dichloroquinonechlorimide—from which the quinone was derived, unless it were possible for the para-derivative to pass by isomeric change into the meta-compound. This, however, as shown above, is impossible, as the intramolecular change occurs in the reverse direction—the meta- into the para-derivative.

This being so, I can only conclude that the analyses recorded by Krause for chlorobromanilic acid and its salts are all wrong; that this chemist must have been dealing with the compound

$$C_6Cl_2(OH)_2O_2,2C_6Br_2(OH)_2O_2,$$

and that the dichlorodibromoquinone must have been the para-derivative.

Bromination of Metadichlorobromoquinol.

Metadichlorodibromoquinone is readily obtained as follows:—Metadichlorobromoquinol (m. p. 135°), suspended in carbon tetrachloride (5 parts), is introduced into a strong stoppered bottle, and 1 mol. proportion of bromine, dissolved in carbon tetrachloride, is added. The stopper is then wired down and the bottle heated in a bath of boiling water for 5—6 hours. The liquid portion is decanted, and the product drained at the pump, and finally spread upon a porous tile until most of the hydrogen bromide, and all the carbon tetrachloride, is got rid of; it consists of crude metadichlorodibromoquinol, and usually melts at 220—225°. When repeatedly recrystallised from glacial acetic acid and benzene, it melts at 231—232°, and yields a diacetyl derivative melting at 265—266°.

It is mixed into a paste with water, and oxidised with potassium dichromate and dilute sulphuric acid. The crude quinone is then treated as described above, under the other tetra-halogen quinones, and finally crystallised from glacial acetic acid and benzene. It separates from benzene in six-sided plates, melts at 291°, and closely resembles the para-derivative, but is perhaps a little more soluble. "The crystals are probably monosymmetric, with the axial relations $a:b:c = 1{\cdot}9654:1:0{\cdot}6864$; $\beta = 90°\ 0'$." "The substance is entirely distinct from the compound examined by Levy, to which he assigned the axial relations $a:b:c = 1{\cdot}445:1:3{\cdot}0286$; $\beta = 74°\ 31'$." "The complete crystallographic investigation of the tetra-halogen quinones will be published later."

Analysis of metadichlorodibromoquinone:—

0·2156 gram of substance gave 0·4203 gram of mixed chloride and bromide of silver, and this lost 0·0572 gram on ignition in a current of dry chlorine.

	Calculated. $C_6Cl_2Br_2O_2$.	Found.
Cl........	21·19 per cent.	20·50 per cent.
Br	47·76 ,,	47·77 ,,

Metadichlorodibromoquinone, when treated with alkali, gives chlorobromanilic acid. The sodium salt was obtained in dark, almost black prisms, and crystallographic measurements have already been given for it (see above). Analysis :—

I. 0·207 gram of substance lost 0·0402 gram at 150° and gave 0·0796 gram Na_2SO_4.

II. 0·3939 gram of substance gave 0·3521 gram of mixed chloride and bromide of silver, and this lost 0·0473 gram on ignition in a current of dry chlorine.

III. 0·3987 gram of substance gave 0·3465 gram of mixed chloride and bromide of silver, and this lost 0·0469 gram on ignition in a current of dry chlorine.

	Calculated. $C_6ClBr(ONa)_2O_2$ $+ 4H_2O$.		Found. I.	II.	III.	
H_2O	19·48	per cent.	19·42	—	—	per cent.
Na	12·44	,,	12·41	—	—	,,
Cl........	9·60	,,	—	9·56	9·26	,,
Br	21·65	,,	—	21·58	21·14	,,

The salts of chlorobromanilic acid are much less stable than those of the other anilic acids; they decompose when their aqueous solutions are boiled for a long time, the latter becoming acid; it is therefore necessary, in recrystallising these salts, to previously render the solvent water slightly alkaline.

The potassium salt crystallises in slender, reddish-brown needles. Analysis :—

0·184 gram of substance lost 0·0188 gram at 150°, and gave 0·0879 gram K_2SO_4.

	Calculated. $C_6ClBr(OK)_2O_2 + 2H_2O$.	Found.
H_2O........	9·84 per cent.	10·21 per cent.
K..........	21·34 ,,	21·35 ,,

Chlorobromanilic acid separates on adding an excess of dilute hydrochloric acid to either of its alkali salts in brick-red, flat needles.

Metadichlorodibromoquinol is obtained by reducing the quinone with hydriodic acid and phosphorus. It crystallises from glacial acetic acid or benzene in colourless needles, and, when pure, melts at 231—232°. It is readily soluble in alcohol, but is precipitated from this solvent on the addition of water; it is sparingly soluble in boiling glacial acetic acid, even less so in boiling benzene, very sparingly in boiling water, and practically insoluble in the cold. Analysis :—

0·5628 gram of substance gave 1·1019 gram of mixed chloride and bromide of silver.

	Calculated. $C_6Cl_2Br_2(OH)_2$.	Found.
Cl Br	68·54 per cent.	68·21 per cent.

Diacetylmetadichlorodibromoquinol.—This is prepared by boiling the last-described quinol in a reflux apparatus with acetic anhydride. After crystallisation from glacial acetic acid or benzene, it is obtained in small, colourless needles, and melts at 265—266°. It is very sparingly soluble in glacial acetic acid and benzene at the ordinary temperature, and not very soluble in the boiling liquids. Analysis :—

0·3276 gram of substance gave 0·5079 gram of mixed chloride and bromide of silver.

	Calculated. $C_{10}H_6Cl_2Br_2O_4$.	Found.
Cl Br	54·86 per cent.	54·01 per cent.

Bromination of Metadichloroquinone (low temp.).

When metadichloroquinone (1 mol.) is dissolved in glacial acetic acid (10 parts) and treated with bromine (2 mols.) at a temperature of 15—20°, metadichlorodibromoquinone, mixed with a smaller quantity of paradichlorodibromoquinone, is obtained. The product crystallises from benzene in six-sided plates, and melts at about 292°. Analysis :—

0·2731 gram of substance gave 0·5395 gram of mixed chloride and bromide of silver, and this lost 0·0721 gram on ignition in a current of dry chlorine.

	Calculated $C_6Cl_2Br_2O_2$.	Found.
Cl.........	21·19 per cent.	21·23 per cent.
Br	47·76 „	47·41 „

On decomposing this quinone with sodium hydroxide solution, a salt was obtained, crystallising in dark prisms, and giving numbers on analysis agreeing fairly well with those required for sodium chlorobromanilate, thus :—

I. 0·3725 gram of substance lost 0·0709 gram at 150°, and gave 0·1409 gram Na_2SO_4.

II. 0·268 gram of substance lost 0·0515 gram at 150°, and gave 0·1004 gram Na_2SO_4.

III. 0·2519 gram of substance gave 0·2265 gram of mixed chloride and bromide of silver, and this lost 0·0323 on ignition in a current of dry chlorine.

	Calculated.		Found.			
	$C_6ClBr(ONa)_2O_2 + 4H_2O$.		I.	II.	III.	
H_2O	19·48	per cent.	19·03	19·21	—	per cent.
Na	12·44	,,	12·25	12·13	—	,,
Cl	9·60	,,	—	—	8·81	,,
Br	21·65	,,	—	—	23·06	,,

These numbers do not exhibit as close an agreement with the theoretical as usual, although the utmost care was taken with the various determinations. As before mentioned, the dichlorodibromoquinone, from which the salt was obtained, is a mixture, and consequently the salt must also be a mixture. That the dichlorodibromoquinone is a mixture, is seen by the following experiments:—A portion of the quinone was reduced with hydriodic acid and phosphorus, and the quinol repeatedly crystallised from glacial acetic acid, when a small quantity of a compound melting at 235° (the melting point of paradichlorodibromoquinol) was obtained; whilst, on adding water to the united glacial acetic acid mother liquors, a compound was precipitated which melted at 231° (the melting point of metadichlorodibromoquinol). The former gave a diacetyl derivative melting at 268—269°, and the latter, a similar derivative melting at 265—266°. By fractionally crystallising the dichlorodibromoquinone from benzene, it was resolved into two portions, which gave quinols and diacetyl derivatives exhibiting the same differences in melting point as the last-mentioned. As these experiments were made with fairly large quantities of material, and taking into account the fact that metadichloroquinone yields, exclusively, paradichlorodibromoquinone on brominating it at a high temperature, the inference that the bromination product of metadichloroquinone at a temperature of 15—20° also contains a small quantity of paradichlorodibromoquinone appears to be justified. This work was suggested to me some years ago by Dr. H. E. Armstrong, to whom my best thanks are due.

LIII.—*The Crystalline Forms of the Sodium Salts of Substituted Anilic Acids.*

By William J. Pope.

The crystallographical measurements which are the subject of the present paper were made on substances prepared by Mr. A. R. Ling in the course of his work on the halogen derivatives of quinone (see preceding paper).

The compounds which have been examined are the sodium salts of bromanilic acid, chloranilic acid, and bromochloranilic acid. A molecular compound or double salt composed of two molecular proportions of sodium bromanilate and one of sodium chloranilate was also measured.

Sodium Bromanilate, $C_6Br_2(ONa)_2O_2,4H_2O$.

The crystals of this substance consist of practically opaque, dark-coloured prisms. They attain a length of 6 or 8 mm., and a thickness of about 1 mm. When crushed to powder and the fragments examined microscopically, they are seen to transmit light of a claret colour, and to be strongly doubly refracting. Slight dichroism is also to be observed. The crystals are generally much intergrown with others, and so occur as confused aggregates springing from a common origin. Parallel growths are also frequent. The larger forms, $a\{100\}$ and $b\{010\}$, are conchoidal in character, and so give bad measurements. The form $p\{\bar{1}10\}$, which is generally small in size, mostly gives good reflections; the same is true of $c\{001\}$. The form $m\{\bar{1}01\}$ varies much in size, and is nearly always disfigured by a cavity extending in the direction of the c-axis. This cavity takes the shapes shown in figures 1, 2, and 5, and frequently

FIG. 1.

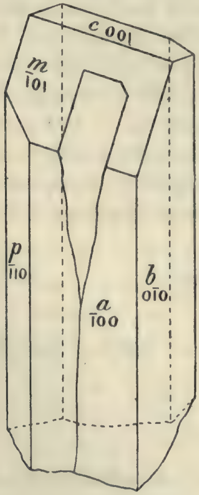
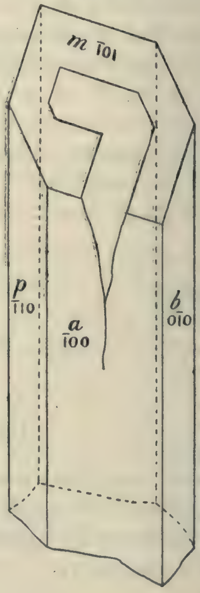


FIG. 2.



almost obliterates the forms $c\{001\}$ and $m\{\bar{1}01\}$. The forms $p\{\bar{1}10\}$ and $c\{001\}$ are often absent. There is a trace of cleavage parallel to $c\{001\}$, but generally the crystals have a very irregular fracture. Twinning on $p\{\bar{1}10\}$ is common. Figures 1, 2, and 5 represent commonly occurring forms of the crystals.

Crystalline system.—Anorthic.

$$a : b : c = 0·8768 : 1 : 0·8100.$$

$$\alpha = 69° 28'; \beta = 87° 56'; \gamma = 71° 49'.$$

Forms present—

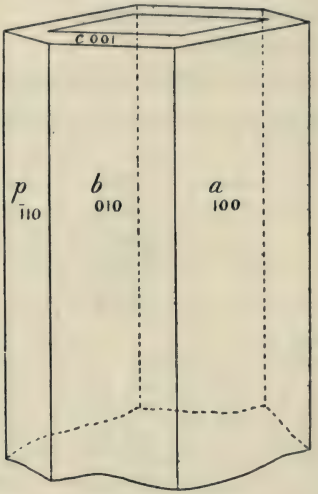
a .... $\{100\}$
b .... $\{010\}$
c .... $\{001\}$
p .... $\{\bar{1}10\}$
m .... $\{\bar{1}01\}$

	Angles.	Number of observations.	Limits.	Mean.	Calculated.
bp	$010 : \bar{1}10$	41	57° 10′—58° 32′	57° 51′	57° 53′
ab	$100 : 010$	44	69 26 —70 11	69 42	—
ap	$\bar{1}00 : \bar{1}10$	43	51 57 —52 48	52 25	—
am	$\bar{1}00 : \bar{1}01$	37	52 41 —53 5	52 52	—
mc	$\bar{1}01 : 001$	34	46 13 —46 53	46 32	46 33
ac	$100 : 001$	35	80 7 —80 54	80 35	—
pm	$\bar{1}10 : \bar{1}01$	7	53 45 —54 27	54 4	53 52
pc	$\bar{1}10 : 001$	4	79 42 —80 17	80 4	79 57
bc	$010 : 001$	26	67 21 —67 52	67 35	—
bm	$0\bar{1}0 : \bar{1}01$	12	86 51 —87 23	87 6	87 0

Sodium Chloranilate, $C_6Cl_2(ONa)_2O_2,4H_2O$.

This substance separates from its hot aqueous solution in very long, dark-coloured prisms, somewhat resembling the bromanilate in appearance. The crystals are, however, much larger than those of sodium bromanilate, and the forms $a\{100\}$ and $b\{010\}$ are very much more conchoidal in character. Isolated crystals are not often found owing to the great tendency which the substance has to crystallise in aggregates or parallel growths. One crop of the crystals consisted of very long, thin, transparent needles which were strongly doubly refracting, slightly dichroic, and transmitted light of a claret-red colour. The face $c\{001\}$ always exhibits a cavity of the shape shown in the figure (Fig. 3); this inclusion sometimes extends to a depth of 2 mm. into the crystal in the direction of the c-axis. The form $p\{\bar{1}10\}$ does not often occur, and when present is small, though brilliant. The reflections obtained from $c\{001\}$ are generally poor owing to the presence of the inclusion mentioned above. No twinning was observed, but there is an imperfect cleavage parallel to $c\{001\}$. The length of the c-axis is indeterminate, owing to the absence of any form which could serve for its measurement.

FIG. 3.



Crystalline system.—Anorthic.

$$a : b : c = 0{\cdot}8743 : 1 : ?.$$

$$\alpha = 88^\circ\ 8'; \ \beta = 89^\circ\ 51'; \ \gamma = 72^\circ\ 30'.$$

Forms present—

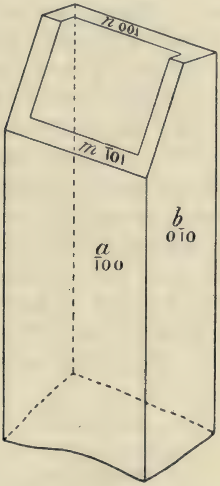
a .... $\{100\}$
b .... $\{010\}$
c .... $\{001\}$
p .... $\{\bar{1}10\}$

	Angles.	Number of observations.	Limits.	Mean.	Calculated.
bp	$010 : \bar{1}10$	14	58° 9′—59° 23′	59° 11′	58° 58′
ap	$\bar{1}00 : \bar{1}10$	17	48 12—48 47	48 33	—
ab	100 : 010	16	72 8—72 53	72 29	—
ac	100 : 001	18	88 56—89 28	89 15	—
ac	$\bar{1}00 : 001$	12	90 21—90 53	90 36	90 45
bc	010 : 001	21	87 29—88 18	87 59	—
bc	$0\bar{1}0 : 001$	7	91 48—92 40	92 2	92 1

Sodium Bromochloranilate, $C_6BrCl(ONa)_2O_2,4H_2O$.

The crystals of this substance are very unsatisfactory for goniometrical measurement; consequently the dimensions given below are only approximate. The crystals consist of small, distorted prisms, dark in colour; when crushed to powder, they are found to be strongly doubly refracting, and slightly dichroic, like the crystals of the two preceding substances. The forms $a\{100\}$ and $b\{010\}$ are very conchoidal in character, and the forms $m\{\bar{1}01\}$ and $c\{001\}$ are mostly practically obliterated by the cavity shown in the figure (Fig. 4). This cavity generally occupies almost the whole of the end of the prism, leaving merely a thin, semitransparent wall with jagged edges. The crystals of this substance are much more brittle than those of the bromanilate and chloranilate, and require great care in handling. The form $p\{\bar{1}10\}$ is seldom present, but is very bright, and gives good images. There is a poor cleavage parallel to $c\{001\}$. No twinning was observed.

FIG. 4.



Crystalline system.—Anorthic.

$$a : b : c = 0{\cdot}888 : 1 : 0{\cdot}814.$$

$$\alpha = 69^\circ\ 59'; \ \beta = 87^\circ\ 3'; \ \gamma = 71^\circ\ 58'.$$

Forms present—

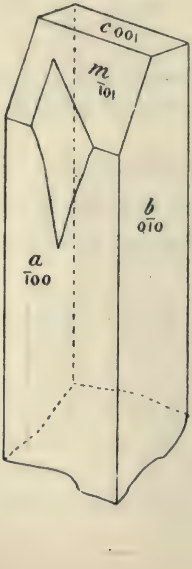
a .... $\{100\}$
b .... $\{010\}$
c .... $\{001\}$
p .... $\{\bar{1}10\}$
m .... $\{\bar{1}01\}$

	Angles.	Number of observations.	Limits.	Mean.	Calculated.
bp	$010:\bar{1}10$	18	56° 59′—57° 52′	57° 29′	57° 33′
ab	$100:010$	17	69 2—70 4	69 36	—
ap	$\bar{1}00:\bar{1}10$	18	52 34—53 8	52 51	—
am	$\bar{1}00:\bar{1}01$	7	53 14—53 47	53 28	—
mc	$\bar{1}01:001$	4	46 32—47 6	46 50	46 41
ac	$100:001$	10	79 22—80 24	79 51	—
bc	$010:001$	5	67 30—68 2	67 49	—

Double Salt of Sodium Chloranilate and Bromanilate,
$2C_6Br_2(ONa)_2O_2,4H_2O + C_6Cl_2(ONa)_2O_2,4H_2O$.

Two samples of this salt were examined: the first, A, being the product of the action of caustic soda on paradichlorodibromoquinone, whilst the second lot of crystals, B, was obtained by simply crystallising a mixture of the chloranilate and bromanilate in the requisite proportions from water. The measurements, as will be seen below, fully prove the identity of the products obtained in these two ways. The crystals consist of large, almost black prisms, which are more brittle than those of sodium bromanilate, but less so than those of the chloranilate. They are indistinguishable from the crystals of sodium bromanilate by mere outward inspection, but the measurements show that there is really a slight difference in geometrical properties between the two substances. The crystals have the form shown in Figs. 1, 2, and 5. Twinning occurs on $p\{\bar{1}10\}$ as in the

FIG. 5.



case of sodium bromanilate. The forms $a\{100\}$ and $b\{010\}$ are, in the larger crystals, conchoidal in character; $p\{\bar{1}10\}$ is generally very bright and small, but is frequently absent. The form $m\{\bar{1}01\}$ always shows the curious cavity noted in the crystals of the preceding salts; in this case, the cavity is generally larger than in the crystals of sodium bromanilate. There is a very poor cleavage parallel to $c\{001\}$. This latter form is always very small, but brilliant, and gives good reflections. On crushing and examining the fragments under the microscope, the crystals are seen to be slightly dichroic and strongly doubly refracting. The light transmitted is of a claret colour.

Crystalline system.—Anorthic.

Forms present—

a .... $\{100\}$
b .... $\{010\}$
c .... $\{001\}$
p .... $\{\bar{1}10\}$
m .... $\{\bar{1}01\}$

A:—

$$a : b : c = 0{\cdot}8825 : 1 : 0{\cdot}8163.$$

$$\alpha = 69° 48'; \beta = 87° 14'; \gamma = 72° 11'.$$

	Angles.	Number of observations.	Limits.	Mean.	Calculated.
bp	010 : $\bar{1}10$	35	57° 17″—57° 46″	57° 37′	57° 38′
ab	100 : 010	37	69 19 —70 7	69 52	—
ap	$\bar{1}00$: $\bar{1}10$	35	52 16 —52 56	52 30	—
am	$\bar{1}00$: $\bar{1}01$	28	53 3 —53 8	53 6	—
mc	$\bar{1}01$: 001	19	46 29 —46 59	46 38	46 49
ac	100 : 001	21	79 35 —80 37	80 5	—
pm	$\bar{1}10$: $\bar{1}01$	7	53 32 —54 8	53 57	54 13
bc	010 : 001	17	67 38 —67 55	67 45	86 58
bm	0$\bar{1}$0 : $\bar{1}01$	9	86 34 —87 6	86 45	—
bm	010 : $\bar{1}01$	1	—	93 23	93 2

B:—

$$a : b : c = 0{\cdot}8825 : 1 : 0{\cdot}8143.$$

$$\alpha = 69° 56'; \beta = 87° 7'; \gamma = 72° 11'.$$

	Angles.	Number of observations.	Limits.	Mean.	Calculated.
bp	010 : $\bar{1}10$	39	57° 11′—57° 54′	57° 39′	57° 41′
ab	100 : 010	37	69 34 —70 11	69 51	—
ap	$\bar{1}00$: $\bar{1}10$	41	52 23 —52 41	52 28	--
am	$\bar{1}00$: $\bar{1}01$	25	53 4 —53 17	53 12	—
mc	$\bar{1}01$: 001	14	46 21 —46 59	46 41	46 48′
ac	100 : 001	23	79 36 —80 25	80 0	—
pm	$\bar{1}10$: $\bar{1}01$	9	53 47 —54 19	54 2	54 21
bc	010 : 001	18	67 41 —68 7	67 51	—
bm	0$\bar{1}$0 : $\bar{1}01$	4	86 28 —87 12	86 41	86 58

The mean axial relations are—

$$a : b : c = 0{\cdot}8825 : 1 : 0{\cdot}8153.$$

$$\alpha = 69^\circ\ 52'\,;\ \beta = 87^\circ\ 10\tfrac{1}{2}'\,;\ \gamma = 72^\circ\ 11'.$$

Owing to the very distorted habit of the crystals of the above salts, the constants given cannot possess very great accuracy. This is especially true in the cases of the chloranilate and bromochloranilate, the crystals of which are very irregular, and but few measurements could be made owing to the rare occurrence of some of the forms.

The great similarity between the dimensions of the crystals of sodium bromanilate and those of the double salt is very remarkable. No similar instance could be found amongst organic substances in a search through the literature of the last 10 years or so. Among minerals, the cases of the resemblance of alstonite and barytocelestine to their respective components are somewhat similar, although alstonite is supposed by many mineralogists to be a mere isomorphous mixture of barium and calcium carbonates.

It is worthy of note that this molecular compound of the formula $2C_6Br_2(ONa)_2O_2,4H_2O + C_6Cl_2(ONa)_2O_2,4H_2O$ is the only product that can be obtained from an aqueous solution of the brom- and chlor-anilates. Mr. Ling has endeavoured to prepare isomorphous mixtures of these two salts, but has failed, the salts simply separating as the double compound, whilst the excess of either constituent is deposited later.

Another is thus added to the list of instances of substances which, while undoubtedly possessing great analogy, both from a chemical and a crystallographical point of view, are nevertheless not isomorphous in the ordinary sense: that is to say, sodium bromanilate and chloranilate have not the power, generally possessed by two chemically analogous substances, of crystallising together in non-molecular proportions.

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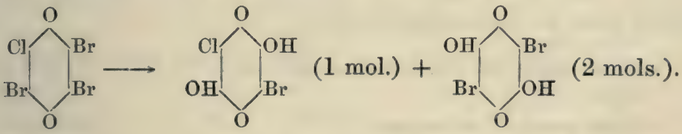
LIV.—*Halogen Derivatives of Quinone.* Part II.

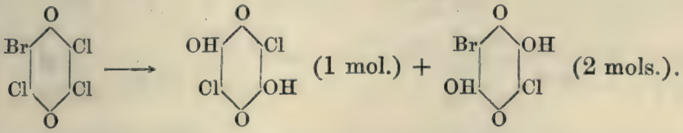
By Arthur R. Ling and Julian L. Baker.

The results described by one of us in the paper preceding, with regard to the action of alkalis on para- and meta-dichlorodibromoquinone, led us to re-examine the behaviour of chlorotribromoquinone and of trichlorobromoquinone towards alkalis.

One of us showed (Trans., 1887, 784) that chlorotribromoquinone, when heated with potassium hydroxide solution, yields chlorobromanilic acid. We have, in one of our experiments, obtained a salt by the action of potassium hydroxide on the quinone, which gave numbers, on analysis, indicating that it was potassium chlorobromanilate; but, although in some subsequent experiments we followed the same conditions as closely as we were able, and in others varied them, we obtained, in every other case, both by the action of potassium and sodium hydroxide, a compound consisting of chlorobromanilate (1 mol.) and bromanilate (2 mols.), thus:—



Trichlorobromoquinone, according to Levy and Schultz (*Annalen*, **210**, 163), yields chlorobromanilic acid when treated with potassium hydroxide. In all our experiments, however, we obtained a uniform product, consisting of chloranilate (1 mol.) and chlorobromanilate (2 mols.), thus:—



We cannot, of course, say that Levy and Schultz were wrong, for, although the reaction has been studied under a variety of conditions, we may not have been successful in obtaining those necessary for the production of chlorobromanilic acid as sole product. We may here remark that, according to the data we have collected (see also Part I), at least 3 mols. of the tetra-halogen quinones appear to be simultaneously concerned in their interactions with alkalis.

Chlorotribromoquinone.—This compound has already been described by one of us (Trans., 1887, 783), when it was obtained by the action of bromine on dichlororthonitrophenol, and on orthochloroparabromorthonitrophenol. It is prepared by dissolving monochloroquinol (1 mol.) in glacial acetic acid (10 parts) and dropping bromine (3 mols.) into the solution heated to 60°. After remaining for some hours, a small quantity of nitric acid may be advantageously added, and the product thrown into water. The precipitated compound is collected, washed, and suspended in dilute sulphuric acid, and triturated with potassium dichromate solution to oxidise any quinol which may be present. Chlorotribromoquinone may be even more readily prepared by brominating monochloroquinone; whereas, however, monochloroquinol is obtained with great ease in a state of purity by passing hydrogen chloride through a solution of quinone (10 grams) in dry chloroform (300 c.c. See Levy and Schultz, *Annalen*, **210**, 138), its conversion into monochloroquinone often involves loss. (For the oxidation of monochloroquinol, see Levy and Schultz, *loc. cit.*, 145.) Chlorotribromoquinone, after crystallisation from glacial acetic acid or benzene, melts at 292°. The melting point of some of the original specimen from the nitrophenols was found to be the same. It separates from its solution in benzene in large, six-sided plates. Analysis gave the following results:—

I. 0·2726 gram of substance, dried at 100°, gave 0·1906 gram CO_2.

II. 0·1860 gram of substance, dried at 100°, gave 0·3453 gram of mixed chloride and bromide of silver.

III. 0·2185 gram of substance, dried at 100°, gave 0·4035 gram of mixed chloride and bromide of silver, and this lost 0·0770 gram on ignition in a current of dry chlorine.

		Calculated. $C_6ClBr_3O_2$.		Found.			
				I.	II.	III.	
C............		18·97	per cent.	19·10	—	—	per cent.
Cl	72·58	9·34	,,	—	72·28	8·85	,,
Br		63·24	,,	—		63·35	,,

As mentioned above, in one experiment we obtained, by the action of potassium hydroxide on chlorotribromoquinone, as sole product, chlorobromanilic acid. This was conducted as follows:—The quinone was heated at 80° with a 5 per cent. solution of potassium hydroxide. The salt was twice recrystallised from water, and obtained in dark-red needles. Analysis:—

I. 0·2012 gram of substance lost 0·0195 gram at 150°.

II. 0·2662 gram of substance lost 0·0257 gram at 150°, and gave 0·1248 gram K_2SO_4.

III. 0·1958 gram of substance gave 0·1761 gram of mixed chloride and bromide of silver, and this lost 0·0247 gram on ignition in a current of dry chlorine.

	Calculated.	Found.			
	$C_6ClBr(OK)_2O_2$ + $2H_2O$.	I.	II.	III.	
H_2O........	9·84 per cent.	9·70	9·66	—	per cent.
K..........	21·34 ,,	—	21·01	—	,,
Cl.........	9·71 ,,	—	—	9·07	,,
Br.........	21·88 ,,	—	—	22·68	,,

In the remaining experiments, which yielded the compound of chlorobromanilic and bromanilic acid, 5 per cent. aqueous alkali (potash or soda) was used in some cases, and 3 per cent. alkali in others. The following results were obtained on analysing the salts:—

Sodium Salt.—Large, dark-red, almost black prisms.

0·2129 gram of substance lost 0·0379 gram at 150°, and gave 0·078 gram Na_2SO_4.

	Calculated. $C_6ClBr(ONa)_2O_2,2C_6Br_2(ONa)_2O_2$ + $12H_2O$.	Found.
H_2O............	18·03 per cent.	18·09 per cent.
Na.............	11·51 ,,	11·87 ,,

Potassium Salt.—Flat, red needles; the colour of this salt is much lighter than any of the other potassium salts examined. Analysis:—

I. 0·2349 gram of substance lost 0·0221 gram at 150°, and gave 0·1032 gram K_2SO_4.

II. 0·1884 gram of substance gave 0·0822 gram K_2SO_4.

III. 0·3911 gram of substance gave 0·3579 gram of mixed chloride and bromide of silver.

IV. 0·2907 gram of substance gave 0·2627 gram of mixed chloride and bromide of silver.

	Calculated.	Found.				
	$C_6ClBr(OK)_2O_2,2C_6Br_2(OK)_2O_2$ + $6H_2O$.	I.	II.	III.	IV.	
H_2O....	9·11 per cent.	9·40	—	—	—	per cent.
K......	19·73 ,,	19·69	19·55	—	—	,,
Cl, Br ...	36·73 ,,	—	—	36·77	36·32	,,

Sodium chlorobromanilate and bromanilate were mixed in the requisite proportion to form this compound, and twice crystallised from boiling water. Analysis:—

0·1678 gram of substance lost 0·0299 gram at 150°, and gave 0·0605 gram Na_2SO_4.

	Calculated. $C_6ClBr(ONa)_2O_2,2C_6Br_2(ONa)_2O_2 + 12H_2O$.	Found.
H_2O.........	18·03 per cent.	17·81 per cent.
Na..........	11·51 ,,	11·67 ,,

Chlorotribromoquinol is prepared by reducing the quinone with hydriodic acid and phosphorus; it agrees with the description previously given by one of us (*loc. cit.*), and melts at 234°; the diacetyl derivative, however, melts at 275°, and not at 263°, as stated. We have re-determined the melting point of the original specimen, and found it to be 273°, so that the value 263° was, doubtless, a clerical error.

Trichlorobromoquinone was prepared by brominating trichloroquinone in glacial acetic acid solution at about 100°. It is purified by crystallisation from benzene or glacial acetic acid. It melts at 290°, and separates from its solution in benzene in yellow, six-sided plates. Analysis gave the following results:—

I. 0·1016 gram of substance gave 0·219 gram of mixed chloride and bromide of silver, and this lost 0·0155 gram on ignition in a current of dry chlorine.

II. 0·162 gram of substance gave 0·3404 gram of mixed chloride and bromide of silver.

		Calculated. $C_6Cl_3BrO_2$.	Found. I.	Found. II.
Cl	64·19	36·66 per cent.	37·29	63·35 per cent.
Br		27·53 ,,	27·31	

When trichlorobromoquinone is treated with 5 per cent. alkali, it yields the above-mentioned compound of chloranilic and bromanilic acids. The following analytical data were obtained with the sodium salt:—

The salt crystallises with $10\frac{1}{2}$ mols. H_2O in magnificent, dark-red, almost black, prisms.

I. 0·2249 gram of substance lost 0·0413 gram at 150°, and gave 0·0926 gram Na_2SO_4.

II. 0·2704 gram of substance lost 0·05 gram at 150°, and gave 0·1099 gram Na_2SO_4.

III. 0·2336 gram of substance gave 0·2171 gram of mixed chloride and bromide of silver.

IV. 0·3923 gram of substance gave 0·3590 gram of mixed chloride and bromide of silver.

	Calculated. $C_6Cl_2(ONa)_2O_2,2C_6ClBr(ONa)_2O_2 + 10\frac{1}{2}H_2O$.	Found.				
		I.	II.	III.	IV.	
H_2O....	18·32 per cent.	18·36	18·49	—	—	per cent.
Na.....	13·30 ,,	13·33	13·12	—	—	,,
Cl Br ...	29·11 ,,	—	—	29·53	29·08	,,

Sodium chloranilate and chlorobromanilate were next mixed in the above proportion, and twice crystallised from boiling water. The salt was similar in appearance to that just described. Analysis:—

I. 0·1946 gram of substance lost 0·0356 gram at 150°, and gave 0·0798 gram Na_2SO_4.

II. 0·2906 gram of substance gave 0·2663 gram of mixed chloride and bromide of silver.

	Calculated. $C_6Cl_2(ONa)_2O_2,2C_6ClBr(ONa)_2O_2 + 10\frac{1}{2}H_2O$.	Found.		
		I.	II.	
H_2O.......	18·32 per cent.	18·29	—	per cent.
Na........	13·30 ,,	13·28	—	,,
Cl Br	29·11 ,,	—	29·13	,,

Trichlorobromoquionol is obtained by reducing the quinone with hydriodic acid and phosphorus. It crystallises from benzene in colourless, flat needles, and melts at 230—231°; Levy and Schultz (*loc. cit.*) record 229°.

Diacetyltrichlorobromoquinol was obtained from glacial acetic acid in white needles melting at 261—262°, but the following analytical values, which are in agreement with one another, indicate that it was not pure:—Calculated, Cl + Br 49·52 per cent. Found, 48·52 per cent. and 48·39 per cent.

LV.—*The Hydrolytic Functions of Yeast.* Part I.

By James O'Sullivan.

Berthelot was the first to show that the hydrolysis of cane sugar by yeast was due to a "soluble ferment" contained in the yeast cells, and in 1860 (*Compt. rend.*, May) he showed that the water in which yeast was washed possessed the same power, and that the soluble substance to which this was due could be precipitated by means of alcohol from its solutions without losing its activity. No matter where one turns to look up this subject, the substance of Berthelot's discovery is invariably stated. When speaking of yeast water, it appears that those who have worked on the subject have not taken into consideration the condition or health of the yeast employed; whether the yeast was alive or dead, young or old, seems not to have been considered. Now, knowing as we do, that dead or softened yeast (yeast kept till it liquefies) readily yields its invertase to water, and that there must be stages in this softening process; it is most important to keep in mind the question of the age of the yeast, and the manner in which it has been kept, when we are dealing with its hydrolysing power or that of its water extract. There can be no doubt whatever that by prolonged contact with water, as already shown by Fernbach (*Ann. Inst. Pasteur*, **9**, 1890), invertase is extracted from yeast, but we cannot look upon such extracted yeast as healthy. It appears from Fernbach's work that, by prolonged washing with water, yeast can be completely exhausted of its invertase.

When we come to study the life functions of yeast, and, I take it that the hydrolysing action is one of these, we must work with the yeast as a living organism in full possession of its well-known life functions. It is with such a yeast that I propose to show in this Part I of my paper:—

I. That healthy yeast yields none of its invertase, or hydrolytic power, to water in which it is washed.

II. That when healthy yeast is placed in contact with a cane-sugar solution, the hydrolysis that takes place is solely an action "under the immediate influence of the plasma of the cell," and that "no" invertase leaves the yeast cell during the time that the hydrolysis is being effected.

Preparation of Yeast.

The yeast employed in the following experiments was collected at Messrs. Bass and Co.'s Breweries on the second day of fermentation. Every cell of this yeast possessed all the visual appearances which an experienced observer of yeasts associates with young and healthy yeast. What I mean by healthy, in the sense in which I wish to have it understood, is a yeast capable of growing and performing the ordinary technical requirements in an efficient manner under the usual technical conditions.

A quantity of liquid yeast was mixed with a large bulk of distilled water, and after allowing the mixture to stand for 5—10 minutes, the top portion was decanted off from the heavier or more quickly subsiding part. This operation was repeated three or four times, each time neglecting the more rapidly subsiding deposit which contains other matters than yeast. The supernatant liquid with the yeast in suspension was then filtered through a linen towel, and the yeast left on the towel was freed as much as possible from water by gentle pressure. Yeast thus prepared was found to contain about 25 per cent. of dry substance, of which from 55 to 60 per cent. is albumin if calculated from the nitrogen found by multiplying by 6·25. That yeast does not contain this amount of albumin there can be no question.

It may appear at first sight that there would be very little difficulty in ascertaining, one way or the other, whether yeast gave up its invertase or hydrolysing substance to water or to a cane sugar solution; on investigating this question, however, it was found to be not as easy as it appeared at first sight.

The first step was to filter out the yeast so that the water extract or filtrate could be tested for hydrolytic power. Filtering through a number of filter papers did not remove the yeast cells. On adding aluminium hydrate to the mixture of yeast and water and well shaking, a filtrate was invariably obtained which was absolutely bright and free from yeast, and similar filtrates were obtained when a trace of finings or plaster of Paris was employed. For reasons which I shall now refer to, the addition of these substances to the yeast and water, or to the yeast and sugar solution, had to be abandoned.

Before any substance could be used to "catch up" the yeast cells in order to prevent them going through the filter paper, it was necessary first to prove that, if invertase were present, no matter how small the quantity, the substance used in the filtration had no influence on the invertase. I was compelled to decide this question from the fact that when any yeast, no matter how obtained, was suspended in water, or in a cane sugar solution in which partial inversion was allowed to take place, and aluminium hydrate was employed in filtering the yeast, the filtrates thus obtained invariably showed no evidence of the power of invertase. This, considering that the yeast employed in my earlier experiments was of various ages, and from different sources, was, I thought, too conclusive as to the yeast not parting with its invertase.

That aluminium hydrate, gypsum, and finings, the substances I first employed to catch up the yeast cells, have a retarding influence on the hydrolytic action of invertase will be clearly seen from the following experiments.

The aluminium hydrate used was prepared by precipitating alum with ammonia and washing the precipitate, first by decantation, and then on a filter, until the washings gave no reaction for sulphuric acid, and only gave the faintest indication of ammonia with Nessler's reagent. This washing process takes many days.

Retarding Influence of Aluminium Hydrate.—5 grams of cane sugar were dissolved in water and 0·2 c.c. of an invertase solution was added, then the solution was made up to 100 c.c.

a. To 50 c.c. of this solution 0·1 c.c. of decinormal sulphuric acid was added. This was halved, and to one-half (*c*) a little aluminium hydrate was added, and after mixing well, it was filtered; the other half (*d*) was simply filtered.

b. The unacidified 50 c.c. was halved in the same way as "*a*" and the halves "*e*" and "*f*" treated like "*c*" and "*d*."

These filtrates were laid aside under the same conditions in a cool place for 24 hours, and the optical activities of the solutions were then observed to be as follows:—

c. 200 mm. tube = 10·2 divs.
d. ,, ,, = −4·6 ,,
e. ,, ,, = 14·0 ,,
f. ,, ,, = −4·6 ,,
Original 5 per cent. solution = 19·2 ,,

To 100 c.c. of cane sugar solution sp. gr. 1019·4, and having an opticity, 100 mm. tube (Soleil-Ventzke-Scheibler being the polariscope employed), 9·6 divs., a few drops of invertase solution was added, and after well mixing, the solution was halved.

a. To 50 c.c. a little aluminium hydrate was added, and after agitation, the solution was filtered.

b. The remaining 50 c.c. was simply filtered. Both filtrates were laid aside as before for 24 hours, and the opticities of the solutions were then observed to be as follows:—

a. 100 mm. tube = 9·2 divs.
b. ,, ,, = −2·9 ,,

Retarding Influence of Finings.—To 25 c.c. of a 4 per cent. cane sugar solution, one drop of the same invertase was added, and the solution, after well mixing, was halved.

a. One-half had added to it one drop of finings, and after well agitating, it was filtered.

b. The remaining half was simply filtered. Both filtrates were laid aside as before for 23 hours, and the opticities were then observed to be as follows:—

a. 100 mm. tube = 7·8 divs.
b. ,, ,, = 5·4 ,,
Original 4 per cent. solution = 7·7 ,,

Retarding Influence of Plaster of Paris.—This experiment was performed exactly as in the case of finings, only more sugar and less invertase was added, and after 20 hours, the opticities of the solutions were as follows:—

a. 100 mm. tube = 12·5 divs.
b. „ „ = 11·0 „

It is not necessary in these experiments to calculate the amounts of cane sugar inverted under the condition mentioned, it suffices for the object of the experiments to compare the opticities obtained in each condition. It will be readily seen that in the four experiments where the solution of cane sugar containing the invertase had neither aluminium hydrate, finings, nor plaster of Paris added to it, there was a greater inversion, as shown by the fall in the opticity. It will also be seen that in the case of the acidified cane sugar solution, the retarding influence of the aluminium hydrate is not so marked as in the neutral solution.

The amount of aluminium hydrate employed in the above experiments, when dry, would not weigh more than 0·03 to 0·05 gram.

The pulp of Swedish filter-paper was found to have no influence on the hydrolytic action of invertase. About 2 grams of cane sugar were dissolved in 25 to 30 c.c. of water. The opticity of the solution was 100 mm. = 16·2 divs. The whole of this solution was inoculated, if I may so use the word, with four dips of a pin's point of invertase solution. The pin, 1 inch long, was dipped into the invertase solution and then into the sugar solution, this being repeated four times. The solution was now divided, and to one-half (*a*) a pellet of paper pulp was added, and, after well shaking, this and (*b*) the remaining half, were filtered. The filtrates, after 24 hours at 16—17°, were found to have absolutely the same opticities: 100 mm. = 12·1 divs.

To 50 c.c. of a 5 per cent. sugar solution, 0·1 c.c. decinormal sulphuric acid was added, and 0·2 c.c. of the invertase solution. To one-half of this solution a pellet of paper pulp was added, and this, after well agitating, was filtered; the other half was simply filtered. The opticities of these filtrates were found to be the same at the expiration of 24 hours: 100 mm. = 4 divs.

As the paper pulp, besides having no influence on the hydrolytic action of invertase, was found to effectually remove yeast cells from solutions in which they were suspended, a stock of pulp was prepared for use in the following manner:—Some Swedish filter-paper was torn into small pieces, which were put into a wide-mouthed stoppered bottle; the bottle was half filled with distilled water, and the contents well agitated, in order to reduce the paper to a pulp.

The method adopted in all the experiments, which I shall describe in detail, to filter out the yeast, was as follows:—

When at any time a filtrate, free from yeast, was required from any solution in which yeast was suspended, a little of the pulp, previously dried as much as possible by pressing in a towel, was added to the liquid, and, after well shaking, it was filtered through three small filter-papers.

I would have the reader of this part of my work not to pay much attention to the quantitative expression of the hydrolytic power, but simply to the presence or absence of that power in the filtrates. The quantitative expression of the hydrolytic power will be fully dealt with in Part II.

I.—A. *Series of Experiments.*

To 300 c.c. of cold water, which had been previously boiled, 0·5 gram of yeast was added and thoroughly mixed.

a. To 100 c.c. of this yeast mixture 20 grams of finely pulverised cane sugar were added.

b. To another 100 c.c. 10 grams of sugar were added.

c. To the remaining 100 c.c. 5 grams of sugar were added.

When the sugar was dissolved in all three solutions, the yeast cells were counted in the manner devised by Peterson (*Meddelser fra Carlsberg Laboratoriet*, Hefte I) by means of a hæmatimeter, and they were found to be per volume of 1/4000 c.mm. for

a	1·5 cells.
b	1·71 ,,
c	1·65 ,,

d. 2 grams of the same yeast, and at the same time, were mixed in water, and the mixture was made up to about 25 c.c. After standing for 20 hours, this mixture was made up to 100 c.c. and filtered. To 10 c.c. of the filtrate (representing 0·2 gram of yeast) in 100 c.c. measure about 50 to 60 c.c. of a solution, containing 10 grams of sugar, were added, and the solution made up to 100 c.c. After four days, the total amount of inversion in this solution was only 0·15 gram of cane sugar in the 100 c.c.

A, *b*, and *c* experiments were allowed to stand for 20 hours, and then the cells were counted in the standard volume as at the start, and they were for

a	1·7 cells.
b	1·6 ,,
c	1·8 ,,

The countings were made in order to see if, during the progress of the inversion, any increase in the number of the cells had taken place; however, a most casual microscopic observation showed that they did not increase, and that there were no budding cells.

The solutions were now made up to 150 c.c., and the alcohol produced in 100 c.c. of each determined; the remaining 50 c.c. being used for an optical observation. The sp. gr. of the alcohol obtained from the three solutions was the same; the distillate made up to 100 c.c. at 15·5° had a sp. gr. of 999·86 = 0·46 of gravity lost by fermentation, or 0·119 gram in the 20 hours. The sp. gr. of the residues, when made up to 100 c.c. at 15·5, were: for *a*, 1051·95; *b*, 1026·17; and for *c*, 1012·93. Calculated from the loss in opticity of the solutions, allowance being made for the amount fermented on the 150 c.c. of solution, and calculating this as dextrose, the quantities of cane sugar inverted in the 20 hours were: for *a*, 11·63 grams; *b*, 7·8 grams; and for *c*, 4·35 grams. To bring about these quantities of inversion in 20 hours, we have only 0·16 gram of yeast for each quantity, whilst the extract, after 20 hours contact of 0·2 gram of the same yeast in *d*, after four days only inverted 0·15 gram of sugar.

I.—B. *Series of Experiments.*

40 grams of cane sugar were dissolved in cold, but recently boiled, water, and the solution was made up to 100 c.c.

0·4 gram of yeast was well mixed in about 25 c.c. of water, and then made up to 100 c.c. (*f*). This solution was allowed to stand for 30 minutes, and, after well shaking,

a. 50 c.c. of it were added to 50 c.c. of the 40 per cent. sugar solution.

b. To about 15 c.c. of the suspended yeast, and at the same time as "*a*," a pellet of pulp was added and the mixture filtered. To 8 c.c. of this clear and yeast-free filtrate in a narrow, graduated test tube, 8 c.c. of the cane sugar solution were added.

These solutions, together with the remaining portion of the suspended yeast (*f*), were put aside in a water-bath, in which the water was kept running, at a temperature of 16—17°.

At the same time as these solutions were laid aside, 8 c.c. of water were added to 8 c.c. of the sugar solution, and the opticity of this solution was found to be 100 mm. = 38·4 divs. This, then, is the opticity of *a* and *b* at the start of the experiment.

After the digestion had gone on for 266 minutes, about 25 c.c. of "*a*" were filtered, and its opticity and also that of "*b*" were observed.

a. 100 mm. = 31·6 divs.
b. ,, = 38·5 ,,

b was found to have no cupric reducing power.

The filtrates, after observation, were laid aside for 48 hours in the bath, and their opticities, after that time, were found to be unaltered.

From this it will be seen that, with the yeast in contact in *a*, the inversion which had taken place in the 266 minutes ceases when the yeast is filtered out, and that in the *b* there is no inversion whatever.

c. 8 c.c. of the filtrate from *a* at the 266 minutes were raised to boiling, and, after cooling to 15·5°, the solution was made up to 8 c.c. and to this, 8 c.c. of the filtrate from a portion of the suspended yeast (*f*) (266 minutes in contact with water) were added. The opticity of this solution was found to be 100 mm. = 15·7 divs.

d. To another 8 c.c. of the filtrate from *a* (266 minutes), 8 c.c. of water were added.

e. To 8 c.c. of the sugar solution, 8 c.c. of the filtrate from the yeast (*f*), as at *c*, were added.

The solutions *c*, *d*, and *e* were laid aside in the bath, and their opticities were observed after a lapse of 24 and 48 hours, and were found to be :—

c. 100 mm. = 15·7 divs.
d. " = 15·6 "
e. " = 38·6 "

Or neither of these solutions contained invertase, or hydrolytic power, as there was no diminution in the original opticity.

The opticity of "*a*" after 23 hours digestion was found to be 100 mm. = 6·5 divs., or 32 divisions lost, which is equal to 12·35 grams of sugar inverted.

In 23 hours there were 12·35 grams of sugar inverted by the yeast in contact, whilst the water which had been in contact with the same proportional quantity of yeast for 266 minutes had not the slightest hydrolytic power on either the partially inverted sugar or upon the original cane sugar.

The yeast cells in *a* and also in the remaining portion (*f*) of the yeast suspended in water were counted per volume as before, after the 23 hours contact, and they were found to be, for—

a. 2·0 cells per volume.
f. 3·8 " "

It is not necessary to mention that whenever a quantity of either *a* or *f* solution was removed, it was first well agitated so as to insure a thorough mixture of the yeast.

The alcohol produced in *a* in the 23 hours was estimated by distilling 50 c.c. and taking a careful specific gravity, in a 500-grain bottle, of the distillate after making up to 50 c.c. at 15·5°. This weighed 499·97 grains, or may be safely said to contain no alcohol.

When the solutions *c*, *d*, and *e* had stood for 48 hours and showed no alteration in their opticities, they were each inoculated with as much of a solution of invertase as covered the surface of half an inch of the point of a small brass pin. The point of the pin was first dipped into the invertase solution and then into the respective solutions. These, after inoculation, were laid aside for 24 hours, and then their opticities were found to be :—

c. 100 mm. = 13·5 divs.
d. „ = 12·7 „
e. „ = 37·0 „

This shows that the solutions were capable of being inverted if only a trace of invertase were present.

I.—C. *Series of Experiments.*

A 40 per cent. solution of cane sugar was made as before, and 0·8 gram of yeast was treated as in B, series (*f*).

a. To 8 c.c. of a clear and yeast-free filtrate, obtained as at *b* series, 8 c.c. of the 40 per cent. cane sugar solution were added.

b. 50 c.c. of the suspended yeast were added to 50 c.c. of the sugar solution.

a and *b* solutions and the remaining quantity of the suspended yeast were laid aside in a cold water-bath.

After 17 hours about 12 c.c. of *b* was filtered and the opticities of this and *a* were found to be :—

a. 100 mm. = 38·2 divs.
b. „ = 3·6 „

These solutions, after observation, were laid aside for 48 hours, and were found not to have altered in their opticities.

The alcohol was determined in *b* at the 17 hours digestion period, and the amount fermented per 100 c.c., calculated from the alcohol, was only 0·1 gram.

When the remaining portion of the suspended yeast (*f*) had stood for 17 hours in contact with water, about 12 c.c. were filtered.

c. To 8 c.c. of this filtrate, 8 c.c. of the 40 per cent. cane sugar were added.

d. To 8 c.c. of the suspended yeast (*f*), 17 hours contact, 8 c.c. of the 40 per cent. cane sugar were added.

These solutions, after 24 hours digestion, gave the following opticities :—

c. 100 mm. = 38·0 divs.
d. „ = 1·6 „

When the suspended yeast (*f*) had been in contact with the water for two days.

e. 8 c.c. of a filtrate from it were added to 8 c.c. of the 40 per cent. sugar solution; and

g. 8 c.c. with the yeast in suspension were added to 8 c.c. of the sugar solution.

These were laid aside in the water-bath for 24 hours, and then their opticities were found to be :—

e. 100 mm. = 38·0 divs.
g. „ = −2·5 „

Here we have an inversion calculated per 100 c.c. in the case of *g*, in which the yeast had been in contact with water for two days, of 13·8 grams of sugar, whilst in *e*, with the water extract from the same proportion of yeast, two days contact, we get only 0·15 gram of inversion per 100 c.c.

II.—D. *Series of Experiments.*

a. 20 grams of sugar were dissolved in water and the solution made up to 100 c.c. at 15·5°. This solution was poured into a conical measure-glass and 0·8 gram of yeast was added. A current of air was passed through the solution to keep it agitated, and after 47 minutes digestion, about 20 c.c. were removed and roughly divided in two. One portion was simply filtered, the filtrate being received in a small beaker, the other was filtered, but the filtrate was received in a small beaker containing a drop of strong potash. Fifteen minutes after filtration, the opticity of the filtrate containing potash was found to be

100 mm. = 32·0 divs.

The filtrate obtained without potash, and observed 24 hours later, was found to have absolutely the same opticity.

This experiment, filtering with and without potash, was repeated when the digestion had gone on for 242 minutes, and the opticity of the filtrates observed, as before, were found to be the same—

100 mm. = 12·2 divs.

There was not a trace of alcohol in the whole of the remaining portion of the solution after the 242 minutes digestion.

b. 10 grams of sugar were treated as in *a* experiment, and optical observations were made in the same way after one hour and two hours digestion :—

1 hour, 100 mm. = 4·8 divs.
2 hours, „ = 1·7 „

The opticities of the filtrates without potash were found to be the same as those in which potash was used, although they were allowed to stand for 48 hours.

There was not a trace of alcohol in the remaining portion of the solution after two hours digestion.

c. Another 10 per cent. sugar solution employing 0·4 gram of yeast was treated as in *a* and *b*, and optical observations of the filtrates at one, two, and six hours digestion were made as before, with the following results :—

1 hour, 100 mm. = 13·8 divs.
2 hours, ,, = 9·6 ,,
6 ,, ,, = −1·3 ,,

The filtrates obtained without potash were found to have the same opticities as those with it, although they were allowed to stand for 24 hours before the observation was made.

At the sixth hour the solution contained no alcohol.

The experiments given here are only *some* of those that were made in order to decide the question whether invertase left the healthy yeast cell when it inverted cane sugar, or when it was placed in contact with water for a reasonable time; many more were made, and all showed distinctly that it does not. As I shall have occasion to refer to this again in Part II, it is needless to add further proof by way of experiment.

I have never seen a filtrate from a cane sugar solution—5 to 25 per cent.—undergoing inversion with yeast under the conditions mentioned, that showed any definite evidence of the presence of invertase; a loss, after filtration, in the opticity of a filtrate from a solution of sugar undergoing inversion being taken as an index of the presence of invertase, and no loss an index of its absence. If ever a loss in opticity in a filtrate after filtration was observed, and this was not often, the reason was invariably accounted for by the presence of yeast cells in the filtrate.

I shall not go farther back for numbers than those in the last-mentioned experiment *c* (D series), to show that the hydrolytic action of yeast is solely a contact action, or, rather, that it is an action performed under the immediate influence of the plasma of the cell.

In a 100 mm. tube of a Soleil-Ventske-Scheibler polariscope, 10 grams of cane sugar in 100 c.c. of solution gives a rotation of 19·2 divisions, and 10·526 grams of invert sugar a rotation of −6·7 divisions, or 10 grams of cane sugar, after complete inversion, yielding 10·526 grams invert sugar, will show a loss in opticity, the volume of solution being kept constant, of 25·9 divisions, therefore, the loss in opticity per 100 c.c. of a cane sugar solution, inverted either partially or completely by yeast, divided by 2·59—the 100 mm. tube being used—will give, in grams, the amount of cane-sugar which has been inverted.

The quantities of cane sugar inverted in C, calculated from the loss in opticity, are for—

1 hour	2·08 grams.
2 hours......	3·70 ,,
6 ,, ...	7·91 ,,

Here are 7·91 grams of sugar inverted in 6 hours, and yet no invertase was observed to be present in the filtrate at either period of the inversion.

Although I show that when yeast has been in contact with cane sugar there is no evidence of invertase leaving the cell during the progress of hydrolysis, yet that inactive nitrogenous matter, to a small extent, leaves the cell will be seen from the following experiments :—

To 100 c.c. of a 20 per cent. sugar solution, 1 gram of yeast was added, and the inversion conducted as in D series. When the inversion had gone on for two hours (5·6 grams inverted), the yeast was filtered out. 50 c.c. of the filtrate were then evaporated to dryness, the nitrogen in the residue determined by Kjeldahl's method. Calculated as albumin, the nitrogen found amounted to 0·0109 gram on the 100 c.c. (1 gram of yeast). The dry substance in 1 gram of the same yeast was found to be 0·2247 gram, and the albumin contained in this amounted to 0·132 gram (58·7 per cent.). 0·0109 gram having gone into solution, is equal to 8·02 per cent. of the total nitrogenous matter of the yeast.

This experiment was repeated, employing a 30 per cent. sugar solution and 2 grams of yeast, and the albumin was determined in the filtrate when the inversion had gone on for six hours (21·1 grams inverted), and it amounted to 0·012 gram for the 2 grams of yeast. The filtrates from these two experiments, at the stages of inversion mentioned, were put aside for 24 hours, and their opticities were found to remain unaltered, no loss in opticity having occurred after filtration. Had these small quantities of nitrogenous matter been invertase, or the matter to which yeast owes its activity, it is needless to say there would have been a further diminution in the opticities of the filtrates.

The following are the points which I consider I have established in these experiments :—

1. Healthy yeast yields none of its invertase, or hydrolytic agent, to water in which it is washed.

2. When healthy yeast is placed in contact with a cane sugar solution, the hydrolytic action that takes place is an action solely

occurring "under the immediate influence of the plasma of the cell."

3. The hydrolytic action of yeast on cane sugar takes place without increase of yeast, and there is no alcohol formed.

These points will be again referred to in Part II.

4. The hydrolysis of cane sugar, under the influence of yeast, is a case of zymic hydrolysis.

The word zymic, here used with reference to the hydrolytic action of yeast, is taken from Dr. Armstrong, who was the first to advocate this mode of expression (Trans., 1890, **57**, 530).

LVI.—*Corydaline.* Part II.

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SINCE the publication of our first paper on corydaline (Trans., 1892, 244), our attention has been directed to the work of F. Adermann on this subject (*Inaug. Dissert.*, *Dorpat*, 1890; *Chem. Centr.*, 1891, i, 978—979; Abstr., 1891, 1266). Adermann extracted the dried roots of *Corydalis cava** with alcohol, and obtained an acid solution from which he separated three bases by successive treatment with light petroleum, benzene, and chloroform.

The base obtained from the benzene solution, which Adermann designates A, is present in largest quantity, and is, unquestionably, identical with the corydaline which we are engaged in investigating, although Adermann assigns to it a formula differing from that proposed by us. The identity of the two substances will be apparent from the following comparison. Their behaviour towards solvents is identical. Both are dextrorotatory; a 1 per cent. alcoholic solution of Adermann's base A rotating the plane of polarised light 4° 45′, whilst a solution of corydaline of the same strength gives a rotation of 5° 50′. The influence of light and heat on both substances is the same, and Adermann has come to the conclusion, at which we also arrived, that the colouring matter formed by the action of light or heat is a decomposition product of the alkaloïd. The melting point of Adermann's base A is 138°; that of corydaline, 134·5°. The fol-

* *Corydalis cava* is the same species as that from which the alkaloïd supplied to us by Schuchardt was extracted. We referred to it in our first paper under the synonym *C. tuberosa.*

lowing is a comparison of the analyses of the bases and their platinochlorides with the numbers required by our formula :—

	Adermann's base A. Mean result of two analyses.*	Corydaline. Mean result of Dobbie and Lauder's analyses.	Theory for $C_{22}H_{29}NO_4$. Formula proposed by Dobbie and Lauder.
Carbon =	71·28 p. c.	71·37 p. c.	71·16 p. c.
Hydrogen =	7·07 ,,	7·76 ,,	7·81 ,,
Nitrogen =	4·15 ,,	3·82 ,,	3·78 ,,
Oxygen =	17·50 ,,	17·05 ,,	17·25 ,,
	100·00	100·00	100·00

Platinochloride.

	Adermann.	Dobbie and Lauder.	Theory for $C_{22}H_{29}NO_4,H_2PtCl_6$.
Platinum =	17·75 p. c.	16·93 p. c.	16·93 p. c.

Further confirmation of the identity of the two substances is afforded by the difficulty of obtaining the common salts in the crystalline condition. Solutions of the chlorhydride and sulphate become gummy on evaporation, and crystals can only be obtained with great difficulty. Adermann's iodhydride and platinochloride resemble in all particulars the salts already described by us.

Whilst there cannot be any doubt as to the identity of our corydaline with Adermann's base A, we believe that Adermann is in error in identifying his alkaloïd with hydroberberine, or even in supposing any close connection to exist between the two. Even taking into account the third determination of carbon and hydrogen given by Adermann, which we discarded in comparing the two alkaloïds, the mean results of his analyses agree as well with our formula as with that of hydroberberine :

	Adermann. Mean of three analyses.	Theory for Hydroberberine.	Theory for $C_{22}H_{29}NO_4$.
Carbon =	70·97 p. c.	70·38 p. c.	71·16 p. c.
Hydrogen =	6·99 ,,	6·75 ,,	7·81 ,,
Nitrogen =	4·15 ,,	4·11 ,,	3·78 ,,
Oxygen =	17·89 ,,	18·76 ,,	17·25 ,,
	100·00	100·00	100·00

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* Adermann gives three analyses of the base, but as the carbon in one of them differs by nearly 1 per cent. from the mean of the other two, we have left it out of account in making the comparison. The following are Adermann's results :—

I.	Carbon	= 71·13 per cent.	Hydrogen	= 7·12 per cent.
II.	,,	= 71·43 ,,	,,	= 7·03 ,,
III.	,,	= 70·37 ,,	,,	= 6·82 ,,

whilst if we omit the third analysis, Adermann's figures, as already shown, agree very closely with our own. We have carefully compared our corydaline with a sample of pure hydroberberine prepared for this purpose. We find that the melting point of hydroberberine is 165°, or 30° higher than that of corydaline; that whilst the solvents for the two bases are the same, hydroberberine requires for solution six to eight times as much absolute alcohol as corydaline; that hydroberberine is optically inactive; and that its sulphate crystallises without difficulty. If any further proof were needed that corydaline and hydroberberine are essentially distinct, it is to be found in the fact that, whereas berberine, which differs from hydroberberine by 4 atoms of hydrogen, contains only two methoxy-groups (Perkin, jun., Trans., 1889, 88), corydaline, as we shall presently show, contains four.

We have prepared some additional salts of corydaline, of which we shall now give an account.

Corydaline Hydrobromide.—This salt is easily obtained by adding potassium bromide to a solution of the hydrochloride in water. Like the corresponding hydriodide, it is pale yellow. It is almost insoluble in cold, but dissolves easily in hot water, from which it separates, on cooling, in crystals resembling those of the hydriodide. Analyses of this salt, dried at 100°, gave the following results:—

I. 0·3988 gram of the salt gave 0·1658 gram AgBr = 17·68 per cent. Br.

II. 0·3912 gram of the salt gave 0·1642 gram AgBr = 17·74 per cent. Br.

	Found. (Mean of above numbers.)	Theory for $C_{22}H_{29}NO_4,HBr$.*
Bromine =	17·71 per cent.	17·69 per cent.

Corydaline Ethyl Sulphate.—This compound is easily prepared in a state of purity, and, unlike the other salts of corydaline, which are soluble in water, crystallises from its aqueous solution without difficulty. It can be obtained as a white, crystalline precipitate by mixing solutions of sodium ethyl sulphate and corydaline sulphate. It is, however, most easily prepared by adding sulphuric acid to an alcoholic solution of corydaline, evaporating to a syrupy consistency, and adding water, when the solution immediately sets to a crystalline mass. When this is dissolved in hot water and the solution allowed to cool slowly, beautiful, large, colourless, prismatic crystals, containing 1 mol. H_2O, separate out. Corydaline ethyl sulphate dissolves easily in hot water, alcohol, and chloroform, but is only very sparingly soluble in cold water, and is insoluble in ether. The crystals melt at 152·5° to a clear, yellow liquid. The addition of ammonia or of potassium hydrate to their aqueous solution precipitates the corydaline. This salt is very stable, and it is only after long continued boiling of its aqueous solution that any precipitate of barium sulphate is obtained on the addition of barium chloride. Analyses of the ethyl sulphate, dried over concentrated sulphuric acid in a vacuum, gave the following results:—

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* In our first paper, the formula given for corydaline was $C_{22}H_{28}NO_4$, calculated directly from the results of analyses. The addition of an atom of hydrogen, which is necessary to bring the formula into conformity with the law of even numbers, makes no appreciable difference in the figures given in that paper.

I. 0·2912 gram of the salt gave— 0·1859 gram H_2O = 7·09 per cent. H.; 0·6014 „ CO_2 = 56·32 „ C.

II. 0·3025 gram of the salt gave— 0·1866 „ H_2O = 6·85 „ H.; 0·6200 „ CO_2 = 55·89 „ C.

III. 0·4656 gram of the salt gave 0·0895 gram Pt = 2·77 per cent. N.

IV. 0·4579 gram of the salt gave 0·0881 gram Pt = 2·77 per cent. N.

V. 0·4036 gram of the salt gave 0·1968 gram $BaSO_4$ = 6·69 per cent. S.

VI. 0·4294 gram of the salt gave 0·2100 gram $BaSO_4$ = 6·72 per cent. S.

	Found. (Mean of above analyses.)	Theory for $C_{22}H_{29}NO_4 \cdot C_2H_5HSO_4 + H_2O$.
Carbon	= 56·10 per cent.	55·92 per cent.
Hydrogen	= 6·97 „	7·18 „
Nitrogen	= 2·77 „	2·72 „
Sulphur	= 6·70 „	6·21 „
Oxygen	= 27·46 „	27·97 „
	100·00	100·00

The salt loses its water of crystallisation when dried at 100°:—

I. 0·5906 gram of the salt lost 0·0213 gram H_2O = 3·60 per cent. H_2O.

II. 0·2705 gram of the salt lost 0·0091 gram H_2O = 3·36 per cent. H_2O.

	Found. (Mean of above numbers.)	Theory for 1 mol. H_2O.
Water	= 3·48 per cent.	3·49 per cent.

The corydaline in the salt was determined by precipitation with ammonia:—

I. 0·2752 gram of the salt, dried at 100°, gave 0·2050 gram corydaline.

II. 0·4030 gram of the salt, dried over concentrated sulphuric acid in a vacuum, gave 0·2859 gram corydaline.

		Found.	Theory.
I.	Corydaline	= 74·49 per cent.	74·64 per cent.
II.	,,	= 70·94 ,,	72·03 ,,

Action of Hydrogen Iodide on Corydaline.—5 grams of corydaline were boiled in a flask with 160 c.c. of fuming hydrogen iodide, for several hours, using a reflux condenser, which was kept at a temperature of 40—50°. The escaping vapours, after passing successively through the reflux condenser and through potash bulbs filled with red phosphorus suspended in water and heated to 50—60°, were condensed and received in a flask surrounded with cold water. During the experiment, a steady current of carbon dioxide was passed through the apparatus. The distillate was recognised as methyl iodide by its characteristic odour and by its boiling point (43°). The solution remaining in the distilling flask at the end of the operation, on cooling, deposited a yellow, crystalline substance. After decanting off the excess of hydrogen iodide, the precipitate was slightly washed with cold, and dissolved in hot, water, from which, on evaporation, it crystallised in clusters of yellow prisms. The purification of this salt caused much trouble, on account of the difficulty of separating the last traces of iodine set free by the decomposition of the hydrogen iodide. The addition of sulphurous acid invariably caused decomposition. Eventually we obtained the salt in a state of purity by repeatedly recrystallising it from water and pressing the crystals between filter paper. It dissolves easily in water and in alcohol, less easily in ether, and melts with decomposition between 270° and 280°. Its aqueous solution gives a reddish precipitate with ammonia and potassium hydrate, which dissolves in excess of either reagent. Analyses of the salt, dried at 100°, gave the following results:—

I. 0·2314 gram of the salt gave— $\left\{\begin{array}{l}0\cdot4158 \text{ gram } CO_2 = 49\cdot00 \text{ per cent. C.}\\ 0\cdot0983 \;\;,, \;\; H_2O = 4\cdot72 \;\;,, \;\; \text{H.}\end{array}\right.$

II. 0·2401 gram of the salt gave— $\left\{\begin{array}{l}0\cdot4307 \;\;,, \;\; CO_2 = 48\cdot92 \;\;,, \;\; \text{C.}\\ 0\cdot1011 \;\;,, \;\; H_2O = 4\cdot68 \;\;,, \;\; \text{H.}\end{array}\right.$

III. 0·3180 gram of the salt gave 0·07055 gram Pt = 3·20 per cent. N.

IV. 0·3376 gram of the salt gave 0·07475 gram Pt = 3·19 per cent. N.

V. 0·3681 gram of the salt gave 0·1962 gram AgI = 28·79 per cent. I.

VI. 0·3608 gram of the salt gave 0·1913 gram AgI = 28·65 per cent. I.

	Found. (Mean of above numbers.)	Theory. $C_{18}H_{21}NO_4,HI$.
Carbon	= 48·96 per cent.	48·77 per cent.
Hydrogen	= 4·70 ,,	4·96 ,,
Nitrogen	= 3·20 ,,	3·16 ,,
Iodine	= 28·72 ,,	28·64 ,,
Oxygen	= 14·42 ,,	14·47 ,,
	100·00	100·00

This salt appears, therefore, to be the iodhydride of a base derived from corydaline by the substitution of 4 atoms of hydrogen for four methyl groups, and bears the same relation to corydaline that papaveroline and berberoline bear to papaverine and berberine respectively. To preserve the analogy of nomenclature, the base ought, therefore, to be called "corydaloline," but we hesitate to perpetrate such a cacophony, and prefer for the present to call it apo-corydaline, until some more appropriate name is indicated by a fuller investigation of its relation to corydaline.

We have not yet succeeded in obtaining the free base in a form suitable for investigation. It can, however, be separated from the iodhydride by the cautious addition of dilute ammonia or of potassium hydrate. It dissolves in alcohol, forming a blood-red solution, but is insoluble in water and in all the other ordinary solvents. Its solution rapidly reduces silver salts in the cold, and, on evaporation, leaves a gummy residue which shows no tendency to crystallise. It is remarkable that the formula of the free base differs by only 2 atoms of hydrogen from Wicke's formula for corydaline ($C_{18}H_{19}NO_4$), and it is possible that the two substances may really be isomeric. The differences in their solubility and general behaviour show that they are not identical. For the direct determination of the number of methoxy-groups in corydaline, we made use of Zeisel's method, as described in the *Berichte*, **19**, 143. The following results were given by pure corydaline, dried over concentrated sulphuric acid :—

I. 0·2539 gram of corydaline gave 0·6338 gram AgI = 32·96 per cent. (CH_3O).

II. 0·2920 gram of corydaline gave 0·7230 gram AgI = 32·7 per cent. (CH_3O).

III. 0·2519 gram of corydaline gave 0·6320 gram AgI = 33·13 per cent. (CH_3O).

	Found. (Mean of above numbers.)	Theory for four (CH_3O) groups in $C_{22}H_{29}NO_4$.
(CH_3O)	= 32·93 per cent.	33·42 per cent.

Corydaline, therefore, contains four methoxy-groups. The conclusion that all the oxygen in the alkaloïd is combined with methyl was confirmed by our failure to obtain any definite reaction with phenylhydrazine or phosphorus pentachloride.

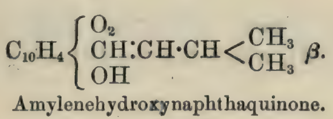
We have not yet completed our experiments on the oxidation of the alkaloïd with potassium permanganate, but we have already obtained evidence of the presence both of a pyridine and a benzene ring.

The physiological action of corydaline is being investigated in Professor McKendrick's laboratory in the University of Glasgow.

LVII.—*The Constitution of "Lapachic Acid" (Lapachol) and its Derivatives.*

By Samuel C. Hooker, Ph.D. (Munich).

The experiments of E. Paternò, published in 1882 (*Gazzetta*, **12**, 337) enabled him to assign to "lapachic acid,"* with a considerable degree of probability, the following formula:—



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH{:}CH\cdot CH<\begin{array}{l}CH_3\\ CH_3\end{array}\ \beta.\\ OH\end{array}\right.$$

Amylenehydroxynaphthaquinone.

The formula was mainly deduced from the following observations:—

1. "Lapachic acid," on distillation with zinc-dust, yields naphthalene and isobutylene.
2. Oxidation with nitric acid gives rise to the formation of phthalic acid in considerable quantity, showing clearly that all the side groups are situated in the same benzene nucleus.
3. On reduction with hydrogen iodide, a hydrocarbon, having the composition of an amylnaphthalene, is formed, differing from the α-amylnaphthylene obtained by Leone (*Gazzetta*, **12**, 209). The amylene chain, therefore, probably occupies the β-position.

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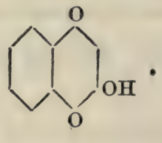
* Lapachic acid is found in a crystalline condition in the grain of a number of South American woods: the lapacho tree, from which the acid derives its name, grows plentifully in the Argentine Republic, yielding a wood which is said to contain as much as 7 per cent. of the acid. The Surinam greenheart, from which the material used in this investigation was mostly obtained, contained a much smaller quantity, probably not more than 1 per cent.

4. "Lapachic acid" forms a monacetyl derivative.
5. Although possessing sufficiently strongly acid properties to expel carbon dioxide from carbonates, experiments failed to reveal the presence of the COOH group.
6. "Lapachic acid," which is yellow, is easily converted by reducing agents into a colourless hydro-derivative. This compound is unstable, absorbs oxygen readily, and becomes reconverted into "lapachic acid."

Although Paternò's experiments did not enable him to decide as to whether lapachol ("lapachic acid") contained the α- or β-quinone group, he expressed himself, in a subsequent publication (*Gazzetta*, **12**, 622), in favour of the former supposition, because lapachone, an isomeric substance, into which lapachol is readily converted, resembled, in his opinion, α- rather than β-naphthaquinone. While Paternò was almost certainly right in assigning the α-quinone group to lapachol, his reason for doing so was insufficient, as I shall show that lapachone is a derivative of β-naphthaquinone, and that, in the conversion of lapachol into lapachone, a change in the quinone group simultaneously occurs. There are, however, several facts which point to the existence of the α-quinone group in lapachol, which Paternò has not advanced, and which it may be well at once to refer to:—

1. Lapachol very closely resembles hydroxy-α-naphthaquinone (naphthalenic acid), which has the following constitution:—

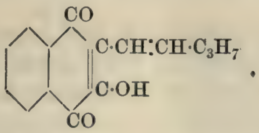


2. Lapachol, like hydroxy-α-naphthaquinone, is *yellow*, whereas β-naphthaquinone and all its simple derivatives are *orange-red*.
3. Lapachol volatilises with steam, although with some difficulty.

It is, therefore, extremely probable that lapachol is a derivative of hydroxy-α-naphthaquinone.

All the experiments to be recorded in this paper point directly and indirectly to the correctness of this conclusion, and justify the substitution of the name lapachol.

The evidence available in regard to the position of the double bond in the amylene side-chain, is at present very limited. It is assumed, however, in this paper, as is most probable, that it is situated as shown in the following formula:—



While much light was thrown by Paternò's investigation on the constitution of lapachol, many of its reactions received no satisfactory explanation. One of the most interesting of the changes which it undergoes is that brought about by concentrated sulphuric acid, which converts it, quantitatively, into the isomeric substance, lapachone, which is entirely devoid of acid properties. This change was first explained by Paternò, by the assumption that 2 mols. of lapachol had combined to form one of the isomeric product; but this view was afterwards shown to be untenable by Paternò and Nasini (*Gazzetta*, **19**, 333), in an investigation on Raoult's law, as the molecular weights of lapachol and lapachone were found, experimentally, to be the same. It was not until some time after the publication of these last experiments that the interaction was first satisfactorily explained by Hooker and Greene (*Amer. Chem. J.*, **11**, 395) in a preliminary paper. It was then shown that the change occurred in two stages, as follows :—

$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH{:}CH{\cdot}C_3H_7\\ OH\end{array}\right. + H_2O = C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2{\cdot}CH(OH){\cdot}C_3H_7\\ OH\end{array}\right.$$

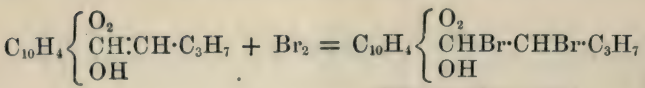
Hydroxyhydrolapachol.

$$= C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2{\cdot}CH{\cdot}C_3H_7\\ O\diagup\end{array}\right. + H_2O.$$

Lapachone.

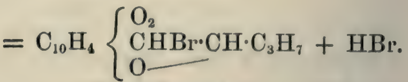
The formation of lapachone from lapachol, as shown in the above equations, rendered it extremely probable that several other changes observed by Paternò occurred in a precisely analogous manner. By the action of bromine on lapachol, Paternò obtained a compound which he believed to be a bromo-derivative of the following constitution, $C_{10}H_4\left\{\begin{array}{l}O_2\\ CH{:}CH{\cdot}C_3H_7.\\ OBr.\end{array}\right.$

This compound, which is insoluble in alkalis, and can be dissolved in, and reprecipitated from, concentrated sulphuric acid in an unaltered condition, was considered by Hooker and Greene (*Amer. Chem. J.*, **11**, 397) to be a lapachone and not a lapachol derivative, the formation of which could be readily explained as follows :—



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH{:}CH\cdot C_3H_7\\ OH\end{array}\right. + Br_2 = C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr\cdot CHBr\cdot C_3H_7\\ OH\end{array}\right.$$

Dibromhydrolapachol.



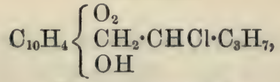
$$= C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr\cdot CH\cdot C_3H_7\\ O\end{array}\right. + HBr.$$

Bromolapachone.

In a paper published some months later, Paternò and Minunni (*Gazzetta*, **19**, 601) adopted this explanation of the formation of lapachone, and recorded some additional facts which they believed added to its weight; but, while admitting that the bromolapachone formula for Paternò's so-called bromolapachic acid had some strong points in its favour, they were not prepared to consider it, on the whole, as probable (*Gazzetta*, **19**, 623).

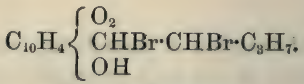
Finally, in a paper published last year (*Gazzetta*, **21**, 374), Paternò and Caberti positively reject the above explanation of the formation of so-called bromolapachic acid, and emphatically assert that the compound cannot be a lapachone derivative. I shall show that Paternò and Caberti have allowed a change which they did not fully understand, and which appeared to be much simpler than was really the case, to mislead their judgment in coming to this decision. The experiments recorded in this paper prove that Paternò's bromolapachic acid is in reality bromolapachone: the compound will, therefore, in future be referred to by the latter name.

The analogy existing between lapachone and bromolapachone is strikingly shown in several reactions: I describe in the following pages the preparation and properties of two compounds obtained by the direct addition of hydrogen chloride and bromide respectively to lapachol, viz.:—



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2\cdot CHCl\cdot C_3H_7,\\ OH\end{array}\right.$$

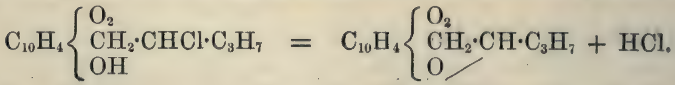
Chlorhydrolapachol.



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr\cdot CHBr\cdot C_3H_7.\\ OH\end{array}\right.$$

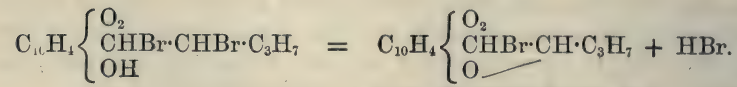
Dibromhydrolapachol.

These compounds in contact with concentrated sulphuric acid are converted into lapachone and bromolapachone respectively, thus:—



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2\cdot CHCl\cdot C_3H_7\\ OH\end{array}\right. = C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2\cdot CH\cdot C_3H_7\\ O\end{array}\right. + HCl.$$

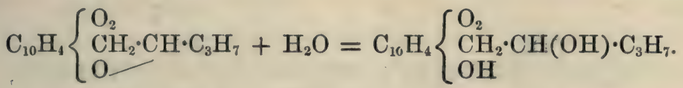
Lapachone.



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr\cdot CHBr\cdot C_3H_7\\ OH\end{array}\right. = C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr\cdot CH\cdot C_3H_7\\ O\end{array}\right. + HBr.$$

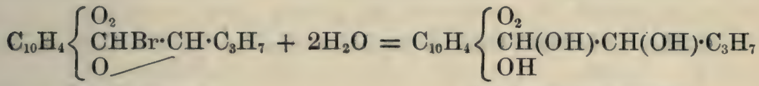
Bromolapachone
(Paternò's bromolapachic acid).

Apart from these changes, the importance of which in deciding the point at issue is readily seen, there are others to which I shall now refer, and which are scarcely less satisfactory or convincing. Boiling aqueous potash converts lapachone into hydroxyhydrolapachol, thus:—



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2\cdot CH\cdot C_3H_7\\ O\diagup\end{array}\right. + H_2O = C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2\cdot CH(OH)\cdot C_3H_7.\\ OH\end{array}\right.$$

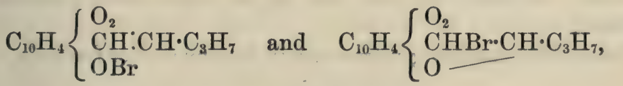
and a precisely analogous change occurs in the case of bromolapachone, which it would be difficult, if not impossible, to explain satisfactorily by Paternò's bromolapachic acid formula.



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr\cdot CH\cdot C_3H_7\\ O\diagup\end{array}\right. + 2H_2O = C_{10}H_4\left\{\begin{array}{l}O_2\\ CH(OH)\cdot CH(OH)\cdot C_3H_7\\ OH\end{array}\right. + HBr.$$

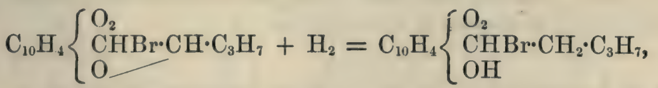
Bromlapachone. Dihydroxyhydrolapachol.

In order to distinguish between the formulæ

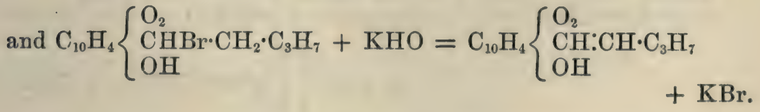


$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH\colon CH\cdot C_3H_7\\ OBr\end{array}\right. \quad\text{and}\quad C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr\cdot CH\cdot C_3H_7,\\ O\diagup\end{array}\right.$$

Paternò and Caberti (*Gazzetta*, **21**, 374) submitted the compound to the action of reducing agents, and found that lapachol, and not lapachone, was formed by the removal of the bromine, thus confirming in their mind the correctness of the bromolapachic acid formula. This reaction, while at first sight apparently antagonistic to the bromolapachone theory, is not, however, really so. The changes as they undoubtedly occur are shown in the following equations: lapachol is not formed by the simple removal of the bromine, but is the result of a secondary change. The change takes place in two stages, thus:—

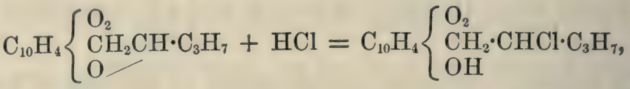


$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr\cdot CH\cdot C_3H_7\\ O\diagup\end{array}\right. + H_2 = C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr\cdot CH_2\cdot C_3H_7,\\ OH\end{array}\right.$$



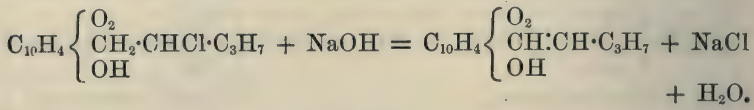
$$\text{and } C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr\cdot CH_2\cdot C_3H_7\\ OH\end{array}\right. + KHO = C_{10}H_4\left\{\begin{array}{l}O_2\\ CH\colon CH\cdot C_3H_7\\ OH\end{array}\right. + KBr.$$

That this is indeed the true explanation of the reconversion of bromolapachone into lapachol is supported by at least two very important facts: 1. Bromolapachone cannot be converted into lapachol by reducing agents in *acid* solution, as Paternò and Caberti themselves found, the alkali being obviously necessary for the removal of the hydrogen bromide in the second stage of the change. 2. Lapachone itself can be reconverted into lapachol by an entirely analogous change. Concentrated aqueous hydrochloric acid readily dissolves lapachone, and under proper conditions soon deposits crystals of chlorhydrolapachol:—



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2CH\cdot C_3H_7\\ O\diagup\end{array}\right. + HCl = C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2\cdot CHCl\cdot C_3H_7,\\ OH\end{array}\right.$$

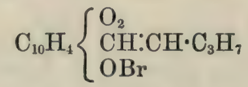
and this compound is instantly converted, in part at least,* into lapachol by the action of dilute sodic hydrate:—



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2\cdot CHCl\cdot C_3H_7\\ OH\end{array}\right. + NaOH = C_{10}H_4\left\{\begin{array}{l}O_2\\ CH{:}CH\cdot C_3H_7\\ OH\end{array}\right. + NaCl + H_2O.$$

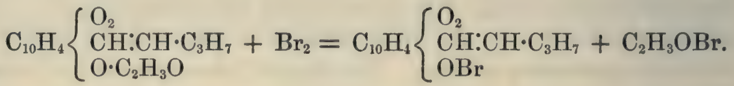
So readily is the hydrogen chloride removed, that the change is instantly effected in the cold by a 1 per cent. solution of sodic hydrate.

Paternò's remaining argument in favour of the formula



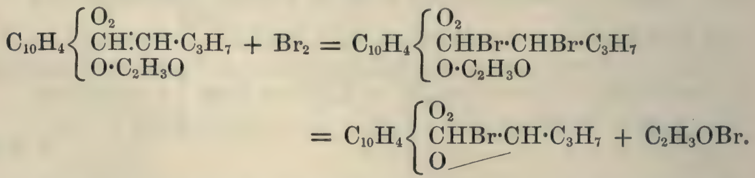
$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH{:}CH\cdot C_3H_7\\ OBr\end{array}\right.$$

is based on the formation of bromolapachone by the action of bromine on the acetyl derivative of lapachol. According to Paternò, action occurs as follows:—



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH{:}CH\cdot C_3H_7\\ O\cdot C_2H_3O\end{array}\right. + Br_2 = C_{10}H_4\left\{\begin{array}{l}O_2\\ CH{:}CH\cdot C_3H_7\\ OBr\end{array}\right. + C_2H_3OBr.$$

but it is at once obvious that the change can be explained equally satisfactorily as shown in the equation:—



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH{:}CH\cdot C_3H_7\\ O\cdot C_2H_3O\end{array}\right. + Br_2 = C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr\cdot CHBr\cdot C_3H_7\\ O\cdot C_2H_3O\end{array}\right.$$

$$= C_{10}H_4\left\{\begin{array}{l}O_2\\ CHBr\cdot CH\cdot C_3H_7\\ O\diagup\end{array}\right. + C_2H_3OBr.$$

I have already shown in the commencement of this paper that there exist strong reasons for regarding lapachol as a derivative of α-naphthaquinone. I shall now enumerate the evidence which is conclusive, showing that lapachone and bromolapachone are derivatives of β-naphthaquinone.

---

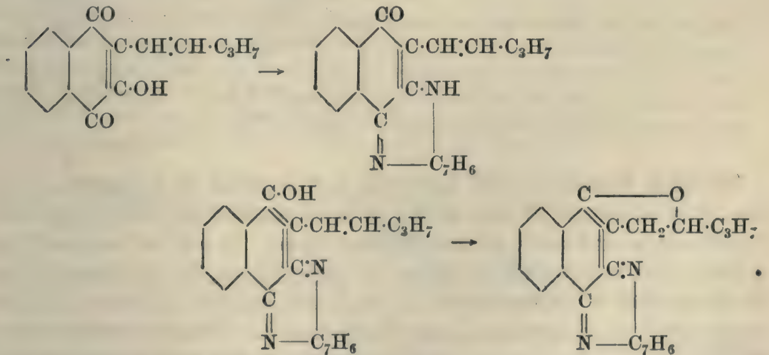
* Hydroxyhydrolapachol and lapachone are simultaneously formed.

- I. Like β-naphthaquinone, lapachone and bromolapachone are *orange-red* substances, whereas α-naphthaquinone, like lapachol, is *yellow*.
- II. Lapachone and bromolapachone are readily acted on by orthotoluylenediamine, forming compounds having all the characteristic properties of the azines.*
- III. Unlike lapachol, lapachone† and bromolapachone do not volatilise with steam.
- IV. Lapachone and bromolapachone are acted on by thiophen and sulphuric acid, giving the characteristic dark-blue compounds similar to those formed under like conditions from orthoquinones (*Gazzetta*, **21**, 377).

The equations therefore, given above, representing the conversion of lapachol and its derivatives into lapachone and its derivatives, while essentially correct as far as they go, do not express the complete change which really occurs. Thus in the conversion of lapachol into lapachone by the action of concentrated sulphuric acid, the change probably occurs in the following steps :—

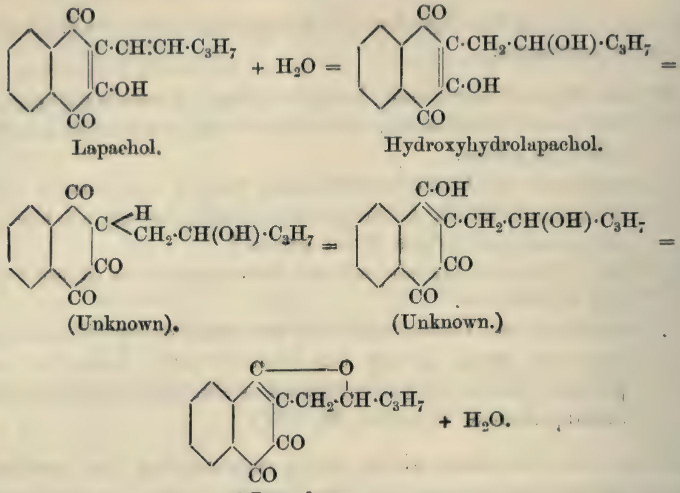
---

* Lapachol yields a compound with orthotoluylenediamine, which crystallises in red needles. This compound is insoluble in alkalis, but, on boiling with dilute sodic hydrate, is converted into a carmine-red substance, probably an eurhodol, soluble in alkaline solutions in the cold, and capable of forming salts with mineral acids. This substance is apparently converted by the action of concentrated sulphuric acid into the same azine as that derived from β-lapachone. These changes are probably correctly illustrated as follows :—



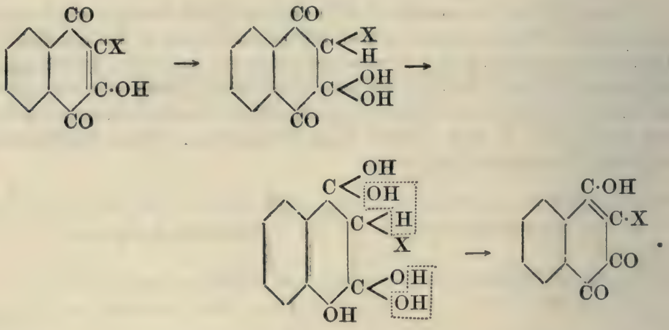
These compounds will be studied in detail and described in a subsequent paper.

† The distillate obtained, in the case of lapachone, is, however, slightly coloured, but no crystals of lapachone separate. With β-naphthaquinone, Liebermann and Jacobson (*Annalen*, 211, 69) also obtained a slightly coloured distillate.

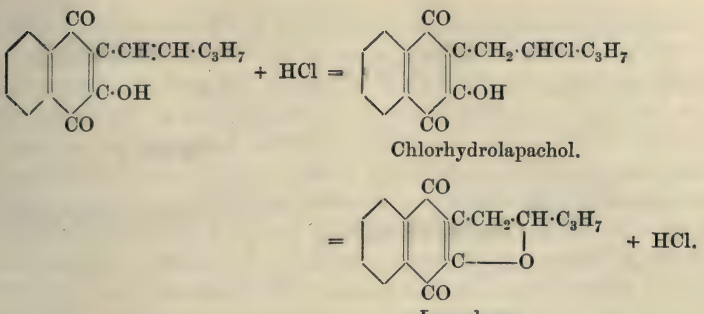


Lapachol. Hydroxyhydrolapachol. (Unknown). (Unknown.) β-Lapachone.

Or possibly the change from hydroxyhydrolapachol to the corresponding β-quinone derivative involves the addition and subsequent splitting off of water, as follows:—



Starting, therefore, with lapachol, a derivative of α-naphthaquinone, it is converted by the action of concentrated sulphuric acid into lapachone, a derivative of β-naphthaquinone. It will be necessary to refer to this compound in future as *β-lapachone*, for the reason that by the action of concentrated hydrochloric acid on lapachol an isomeric product, *α-lapachone*, may be obtained. The difference in the behaviour of concentrated sulphuric acid and hydrochloric acid is indeed a remarkable one, especially as the reactions take place in both cases apparently quantitatively. The action of the hydrogen chloride is as follows:—

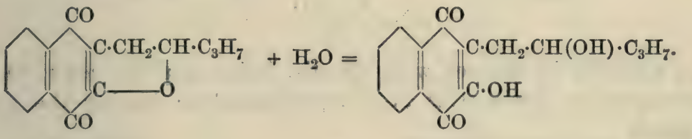


Chlorhydrolapachol.

α-Lapachone.

With concentrated nitric acid,* both α- and β-lapachone are formed; the latter, however, considerably predominates.

The action of boiling alkalis on α- and β-lapachone is extremely interesting. In the case of α-lapachone, the change shown in the following equation occurs:—

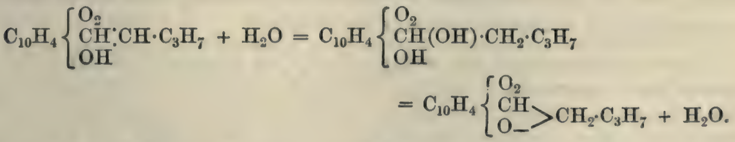


α-Lapachone. Hydroxyhydrolapachol.

With β-lapachone, the same hydroxyhydrolapachol is formed†—

---

* α-Lapachone was first obtained by Paternò (*Gazzetta*, **12**, 371) in small quantity by the action of nitric acid on lapachol: it was also subsequently obtained in traces by Paternò and Minunni (*Gazzetta*, **19**, 616), and by Paternò and Caberti (*Gazzetta*, **21**, 379) in several reactions, in which hydrogen chloride and lapachol or lapachone had taken part. The compound was found by Paternò to be isomeric with β-lapachone. In his earlier papers, no constitution was assigned to it, but subsequent to the publication of Hooker and Greene's investigation (*Amer. Chem. J.*, **11**, 393) explaining the formation of β-lapachone, Paternò and Minunni suggested a similar method of formation for α-lapachone, thus:—

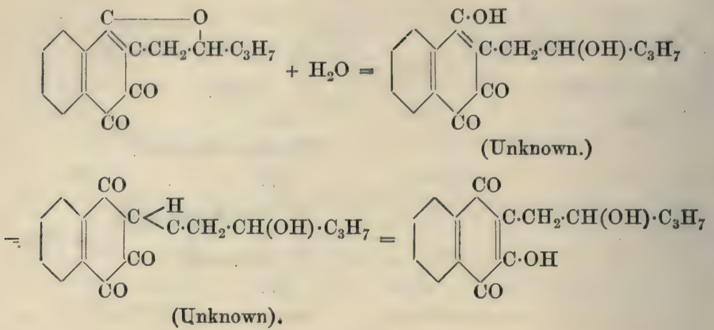


$$C_{10}H_4\left\{\begin{matrix}O_2\\ CH{:}CH\cdot C_3H_7\\ OH\end{matrix}\right. + H_2O = C_{10}H_4\left\{\begin{matrix}O_2\\ CH(OH)\cdot CH_2\cdot C_3H_7\\ OH\end{matrix}\right.$$

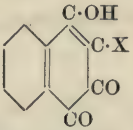
$$= C_{10}H_4\left\{\begin{matrix}O_2\\ CH\\ O-\end{matrix}\right.\!\!>CH_2\cdot C_3H_7 + H_2O.$$

As α- and β-lapachone are, however, converted by boiling alkalis into the same acid, it is obvious that this explanation is not the true one.

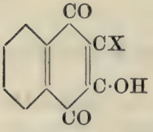
† Nor is this interaction an isolated one: the author has obtained several β-lapachone derivatives, each undoubtedly containing the β-quinone group, and readily convertible by the action of boiling dilute caustic soda or potash into derivatives of lapachol, which, like the latter, contain the α-quinone group.



The conversion of both α- and β-lapachone into the same hydroxyhydrolapachol is in accordance with what appears to be a general rule, namely, that compounds of the general formula

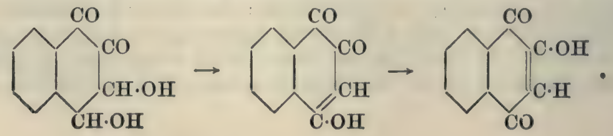

(1)

are unstable in contact with alkalis, being rapidly converted into corresponding derivatives of α-naphthaquinone having the general formula


(2).

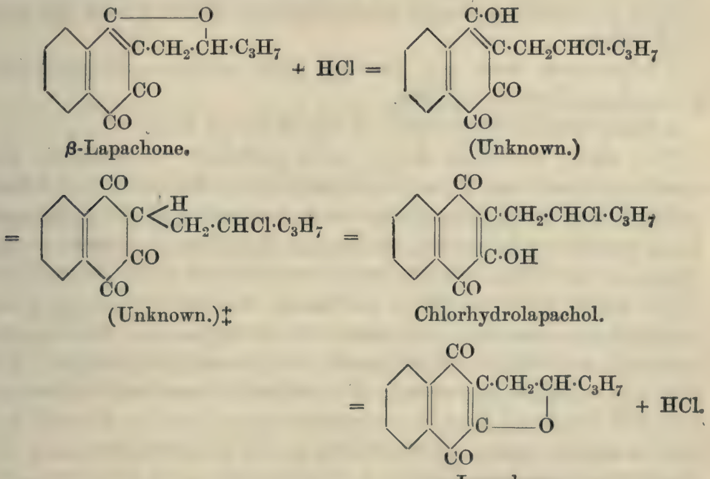
Zincke has shown (*Ber.*, **19**, 2495, 2498) that both β-bromo- and β-chloro-β-naphthaquinone are readily converted into derivatives of α-naphthaquinone by the action of dilute caustic alkalis in the cold. In this case, the halogen-β-naphthaquinone is undoubtedly first oxidised in contact with the alkali, a compound of the general formula (1) given above, being thus produced; and this, in accordance with the rule here laid down, is immediately converted into the corresponding α-naphthaquinone derivative.*

* Since this paragraph was written, Zincke has recorded (*Ber.*, **25**, 1171) the conversion of α-hydroxy-β-naphthaquinone into β-hydroxy-α-naphthaquinone by the action of caustic soda, thus giving one more instance in accordance with the above rule. The α-hydroxy-β-naphthaquinone was not isolated, but undoubtedly existed as an intermediate product in the conversion of dihydroxydiketotetrahydronaphthalene into β-hydroxy-α-naphthaquinone, thus :—



While the ease with which lapachol can be converted quantitatively into either α- or β-lapachone is very remarkable, the fact that these two compounds can be converted into each other, also apparently quantitatively, is still more so. If, for instance, α-lapachone is dissolved in concentrated sulphuric acid, and the solution allowed to stand for a few minutes, water precipitates β-lapachone from it. Similarly, if β-lapachone is dissolved in a comparatively large volume of concentrated hydrochloric acid, α-lapachone* is slowly deposited, until finally, after a few days, little or nothing remains in solution.†

In the conversion of β-lapachone into α-lapachone by hydrogen chloride, I have been fortunate in isolating one of the intermediate products, namely, chlorhydrolapachol,



β-Lapachone. (Unknown.)

(Unknown.)‡ Chlorhydrolapachol.

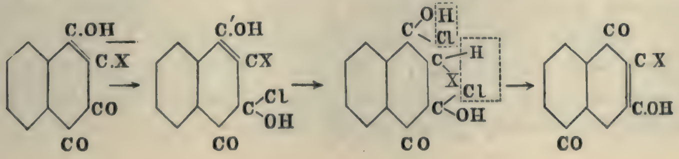
α-Lapachone.

---

* By slightly warming the acid solution, the separation may be considerably hastened. The compound actually deposited is α-lapachone, xHCl, which is immediately decomposed by water into α-lapachone and hydrogen chloride. No importance can be attached to the presence of hydrogen chloride in the compound, as α-lapachone when immersed in concentrated hydrochloric acid forms the same addition product.

† This remarkable difference in the behaviour of sulphuric and hydrochloric acid is not confined, as I shall show in a subsequent paper, to the action of these acids on α- and β-lapachone, but is common to certain derivatives of these compounds.

‡ The conversion of the β-quinone into the α-quinone group may be possibly effected by the successive addition and elimination of hydrogen chloride, thus:—



The importance of the isolation of chlorhydrolapachol and its subsequent conversion into α-lapachone is self-evident. Proof is thereby furnished that in the transformation of β- into α-lapachone the side ring *is opened*, which is entirely in accordance with the above-given theoretical explanation of the change.

That α-lapachone and β-lapachone are really isomers and not polymeric substances, has been proved by the approximate determination of their molecular weights by Raoult's method. Under precisely similar conditions, the figure 265 was obtained for α-lapachone and 261 for β-lapachone.

Like α-naphthaquinone, α-lapachone is yellow, and volatilises with steam.

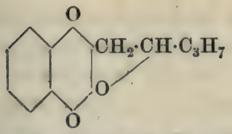
Like β-naphthaquinone, β-lapachone is red, and does not volatilise with steam.

α-Lapachone does not interact with orthotoluylenediamine, but β-lapachone does so readily.

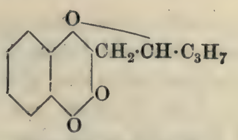
α-Lapachone melts at 117°, β-lapachone at 154°.

The above evidence would seem sufficient to establish the fact absolutely that lapachol and α-lapachone are derivatives of α-naphthaquinone, and that β-lapachone is a derivative of β-naphthaquinone. It is necessary, however, to discuss the matter somewhat more in detail, as the above conclusions do not accord with Paternò's views. Thus, while Paternò gives preference to the α-quinone group for lapachol, he does so, not because of its behaviour, but because of a supposed resemblance of β-lapachone to α-naphthaquinone. Paternò, who has studied the action of hydroxylamine on β-lapachone, was only able to obtain from it a monhydroxime; and as Paternò believed that α-naphthaquinone had only given a monhydroxime, whereas β-naphthaquinone had given a dihydroxime as well, he found in the behaviour of β-lapachone a greater resemblance to that of α- than of β-naphthaquinone. This argument would not, under any circumstances, carry great weight, as Paternò himself realised, but it is deprived of any value whatever by the fact that at the time Paternò wrote (*Gazzetta*, **19**, 622, September, 1889), the dihydroxime of α-naphthaquinone (*Ber.*, **21**, 433, 1888) had, apparently unknown to him, already been discovered.

There is, however, in the work of Paternò, a difficulty apparently more real than the above, which must be explained. By the action of acetic anhydride and sodic acetate on lapachol, Paternò obtained a compound which, on hydrolysis, followed by spontaneous oxidation, gave a quinone (differing from α-lapachone) which he believed to be isomeric with β-lapachone. We have, therefore, β-lapachone and isolapachone most probably, according to Paternò, with the following formulæ, respectively (*Gazzetta*, **19**, 622):—



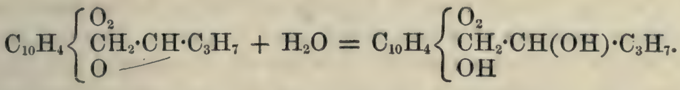
Formula accepted by Paternò as most probable for β-lapachone.



Probable formula for isolapachone (Paternò).

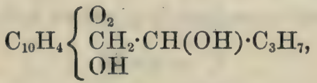
It is at once obvious that the existence of an isolapachone, other than α-lapachone, bearing the relation to β-lapachone shown above, is at variance with the theoretical considerations already discussed. It is easy, however, to prove that Paternò's isolapachone is not related to β-lapachone in this simple way.

It has been already mentioned that when β-lapachone is treated with boiling alkalis, it is converted into hydroxyhydrolapachol, as follows :—



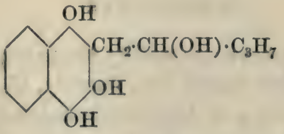
$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2\cdot CH\cdot C_3H_7\\ O\end{array}\right. + H_2O = C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2\cdot CH(OH)\cdot C_3H_7.\\ OH\end{array}\right.$$

Similarly by the action of boiling alkalis on Paternò's isolapachone an intensely red solution is obtained, containing the salt of an acid substance. That the isolapachone is not simply dissolved unaltered, is proved by the fact that ether, in which the isolapachone is readily soluble, does not extract a trace of this substance from the alkaline solution. Hence, if isolapachone has the formula suggested by Paternò, it is necessary to conclude by analogy that the acid substance existing in the alkaline solution has also the composition



$$C_{10}H_4\left\{\begin{array}{l}O_2\\ CH_2\cdot CH(OH)\cdot C_3H_7,\\ OH\end{array}\right.$$

being isomeric with that derived from β-lapachone, and differing only in the nature of its quinone group and the position of its hydroxyl. On treating the two alkaline solutions with zinc-dust, it is evident that, if reduction occur, the same compound must be obtained from both, namely :—



Experiment has shown, however, that this is not the case. After both the solutions were thoroughly reduced, as shown by the entire loss of their intense red colour, they were filtered off from the zinc-dust, and allowed to oxidise spontaneously by absorbing atmospheric oxygen. Acetic acid then precipitated hydroxyhydrolapachol from the solution obtained from β-lapachone, and isolapachone unchanged from the other solution, showing that in the latter case the acid substance first formed probably immediately loses water when liberated from its salts, becoming converted into its internal anhydride; be this as it may, the experiment renders it very improbable that isolapachone possesses the formula assigned to it by Paternò.

An examination of Paternò's analyses of the so-called isolapachone reveals the fact that they agree far better with the formula $C_{15}H_{12}O_3$ than with $C_{15}H_{14}O_3$.

					Calculated.	
	I.	II.	III.	Mean.	$C_{15}H_{12}O_3$.	$C_{15}H_{14}O_3$.
C....	74·38	75·02	74·46	74·62	75·00	74·38
H....	4·98	5·05	5·22	5·08	5·00	5·78

It is at first, indeed, difficult to understand why, in the face of such concordant analyses of a compound easy to purify, Paternò should have chosen the latter formula, in which the theoretical hydrogen is 0·7 per cent. higher than the mean of the analytical results. On comparing the analyses of the diacetyl compound from which isolapachone was obtained, there is the same evidence in favour of the formula $C_{15}H_{12}O_3$, but the results, as stated by Paternò and Minunni (*Gazzetta*, **19**, 607), owing to an error in the theoretical figures, are entirely misleading; and it is probably this error, doubtless due to an accidental interchange of figures subsequent to calculation, which led Paternò and Minunni to select the formula making isolapachone isomeric with β-lapachone.

The mean of Paternò's analysis is given as follows:—

$$C = 69·68$$
$$H = 5·77$$

and above this are given, as the theoretical figures for

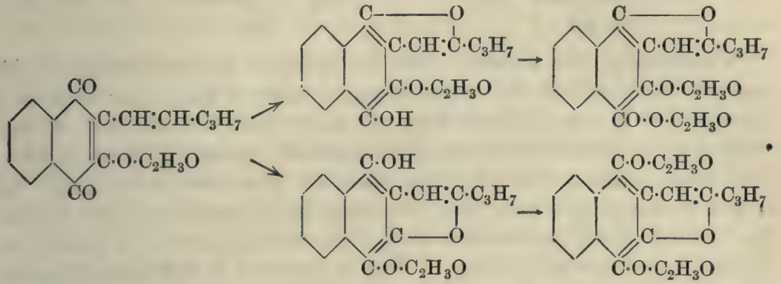
$$C_{15}H_{14}O(OC_2H_3O)_2,$$

$$C = 69·93$$
$$H = 5·52$$

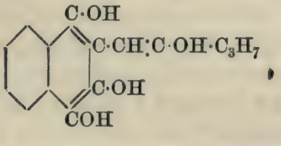
These figures are, however, in reality those required for a compound containing two hydrogen atoms less, namely, $C_{15}H_{12}O(OC_2H_3O)_2$.

The analyses, therefore, of both isolapachone itself and also of the diacetyl compound show clearly that the substances contain two hydrogen atoms less than are present in the formula assigned to them by Paternò and Minunni. Isolapachone is not, therefore, isomeric with lapachone, and the apparent difficulty is thus entirely removed, which the existence of isolapachone, as such, offered to the acceptance of the theory advanced in this paper regarding the relations existing between lapachol, α-lapachone, and β-lapachone.

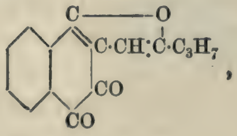
The formation of Paternò's isolapachone can be explained as follows:—By the action of acetic anhydride on lapachol a simple acetyl derivative is first formed, as shown by Paternò (*Gazzetta*, **12**, 358). This compound, in the presence of acetic anhydride and sodic acetate, then probably undergoes the following changes:—



Paternò describes only one acetyl derivative, but Mr. H. W. Shepard, in conjunction with whom I have studied the constitution of isolapachone, has, by following the directions given by Paternò, obtained two isomeric compounds, probably bearing the relation to each other shown in the above formulæ, and, being thus connected in precisely the same way as α- and β-lapachone. On treating the acetyl compounds with caustic alkalis, they both probably yield the same acid substance,



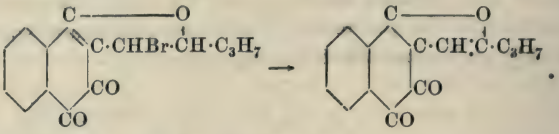
which is, however, spontaneously oxidised, and on acidifying β-naphthaquinonepropylfurfuran,



the so-called isolapachone is obtained.

That this compound is derived from β- and not from α-naphthaquinone, can be at once inferred from its orange-red colour and its general striking resemblance to β-lapachone. We have succeeded in obtaining additional experimental evidence in support of the above formula.

By the action of dilute caustic soda on bromo-β-lapachone, the constitution of which has been fully discussed in the opening pages of this paper, we have obtained, in addition to dihydroxyhydrolapachol, small quantities of Paternò's isolapachone. Thus:—



In accepting this formula, the best possible interpretation would seem to be given of the experimental results so far at our disposal; but when it is remembered that not more than 0·8 per cent. of the compound is formed from bromo-β-lapachone, under the most favourable circumstances, and, further, that all attempts so far made to obtain bromo-β-lapachone from the so-called isolapachone have failed, the formula must be accepted with some caution until it is based on further experimental evidence. The compound is still being studied in my laboratory, and I shall hope to communicate shortly further details of interest concerning it.

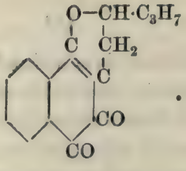
Experimental Part.

The lapachol used in this investigation was principally obtained from Surinam greenheart: a small quantity was also extracted from Bethabarra wood (*Amer. Chem. J.*, **11**, 267).

Surinam greenheart, specially selected from a number of samples for the richness of its yellow grain, was obtained for me from Holland by Messrs. Godfrey S. Saunders and Co., of London, to whom I am much indebted for their trouble and courtesy. The wood, reduced to a fine meal by passage through a disintegrator, was extracted in a 10-gallon percolator essentially as described by the author in conjunction with Dr. Greene in the *American Chemical Journal* (**11**, 268).

Lapachol is formed in small quantity by the action of dilute aqueous alkalis on chlorhydrolapachol (see p. 635); and also by the action of zinc-dust in alkaline solution on bromo-β-lapachone (see p. 642; *Gazzetta*, **21**, 375).

β-Lapachone,



In a preliminary paper published in conjunction with Dr. W. H. Greene (*Amer. Chem. J.*, **11**, 395), it was shown that the conversion of lapachol into lapachone (*Gazzetta*, **12**, 372) by the action of concentrated sulphuric acid probably occurs in two stages, but, as already stated in the introduction to this paper, I have since found that the action is far more complicated than was then supposed, owing to a change which takes place in the quinone group.

Although the intermediate product, hydroxyhydrolapachol, cannot be isolated, it can nevertheless be obtained indirectly by the action of boiling aqueous alkalis on β-lapachone. In contact with dilute mineral acids, it is reconverted into β-lapachone. β-Lapachone is also formed by the action of alkalis, or of concentrated sulphuric acid on chlorhydrolapachol (see pp. 634, 635), and further by the action of concentrated sulphuric acid on α-lapachone (see p. 638).

β-Lapachone is best prepared by dissolving 1 part of lapachol in 5 parts of concentrated sulphuric acid essentially as described by Paternò; as soon as dissolution is complete, the whole is poured into a large volume of water. β-Lapachone separates in a crystalline condition, and can be obtained pure by one crystallisation from alcohol. The yield is quantitative.

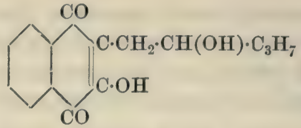
When crystallised from alcohol, β-lapachone usually separates in heavy needles of a brilliant orange-red colour; it is also occasionally deposited from concentrated solutions in irregular, diamond-shaped plates, the surfaces of which are very much striated. The following properties of β-lapachone have not been given by Paternò. β-Lapachone forms two distinct compounds with ammonia, differing from each other in the colour and stability of their salts. These compounds will be studied somewhat more in detail and described at length in a subsequent paper. β-Lapachone readily dissolves in a warm solution of sodium hydrogen sulphite; white, crystalline leaflets are deposited, from which acids and alkalis liberate the original substance.

Concentrated hydrochloric acid dissolves β-lapachone with great readiness, forming an intensely orange-red solution, from which, if not too dilute, first chlorhydrolapachol, and then α-lapachone, is deposited. If water is added to the freshly prepared solution, β-lapachone is reprecipitated for the most part unchanged.

β-Lapachone darkens gradually when exposed to bright daylight. A few minutes exposure to direct sunlight is sufficient to very materially affect its colour.

o-Toluylenediamine and β-lapachone very readily interact in alcoholic solution. The azine thus obtained melts at about 134°; it crystallises readily in bright-yellow needles, and its alcoholic solution exhibits a yellow-green fluorescence. This compound will be described more in detail in a subsequent paper.

Hydroxyhydrolapachol,

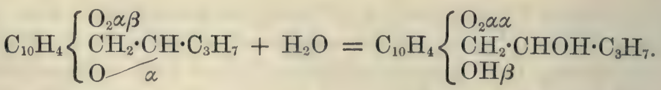


The action of aqueous potash on lapachone has been studied by Paternò (*Gazzetta*, **12**, 372) who writes as follows:—"Lapachone does not dissolve in cold aqueous potash of medium concentration; on heating, it dissolves, forming a fine purple-red solution, which, filtered while hot, deposits, on cooling, beautiful, orange needles of silky lustre, recognised by their melting point (154—155°) to be lapachone. On the addition of hydrochloric acid, the alkaline filtrate yields a precipitate, which, purified by recrystallisation, was similarly found to be lapachone."

This statement is incorrect. The facts are these:—Lapachone dissolves with some difficulty in hot aqueous potash, but in so doing undergoes a change. A new acid compound is formed, and this, and not lapachone, exists in the solution obtained. If hydrochloric acid, in very slight excess, is added to the cold alkaline solution, the new compound separates as a yellow oil, which gradually assumes a crystalline form. If, however, a large quantity of hydrochloric acid be employed, the colour of the turbid solution is seen gradually to change. The bright-yellow gives place to orange, and finally red crystals of lapachone may be observed floating in the liquid.

The new compound has, in fact, been reconverted into lapachone by the excess of hydrochloric acid employed. The experiment has been repeated a number of times, but the author has not once observed the separation of crystals of lapachone from the alkaline solution as described by Paternò.

The action of potash on lapachone is shown in the following equation:—



$$C_{10}H_4\begin{cases}O_2\alpha\beta\\ CH_2{\cdot}CH{\cdot}C_3H_7\\ O\diagup\alpha\end{cases} + H_2O = C_{10}H_4\begin{cases}O_2\alpha\alpha\\ CH_2{\cdot}CHOH{\cdot}C_3H_7.\\ OH\beta\end{cases}$$

β-Lapachone. Hydroxyhydrolapachol.

In order to prepare hydroxyhydrolapachol, 8 grams of lapachone, 4 grams of caustic potash, and 150 c.c. of water are heated together. If the crystals of lapachone be large, they should be first powdered. As the lapachone is dissolved, the colour of the solution becomes very intense, being similar to that of the salts of lapachol.

After boiling several minutes, the solution is filtered to remove any crystals which may have escaped the action of the potash, and an excess of acetic acid is then added. A yellow oil is immediately precipitated, which collects at the bottom of the beaker, and then appears considerably darker than when first seen in a fine state of division. In the course of an hour or so, it solidifies to a yellow, crystalline mass, which, after some hours, may be separated and washed with water. The compound as thus obtained, though slightly coloured at the surface, is in a very nearly pure condition, and can be rendered pure by crystallisation once or twice from alcohol, in which it dissolves very readily and from which it separates slowly in large, yellow, monosymmetric crystals. The yield is theoretical; 8 grams of lapachone gave 8·4 grams of the crude product; that required by theory being 8·59 grams.

The following figures were obtained on analysis :—

I.	0·1965 gram of substance gave	0·4970 CO_2	and	— H_2O.
II.	0·4932 ,, ,,	1·2510 CO_2	,,	0·2743 H_2O.
III.	0·2093 ,, ,,	0·5306 CO_2	,,	0·1160 H_2O.

	Found.			Calculated for
	I.	II.	III.	$C_{15}H_{16}O_4$.
C......	68·96	69·18	69·13	69·23
H......	lost	6·18	6·15	6·15

Hydroxyhydrolapachol melts at 125°. It is readily soluble in most of the ordinary solvents, from which it crystallises after standing some time; if, however, the solvent be allowed to evaporate rapidly, the acid is left as a yellow oil. Under ordinary conditions, it is a very stable substance, and can be crystallised from acetic acid unchanged; but in contact with dilute mineral acids, it is readily converted into β-lapachone, which was identified by its fusing point and other properties, and by analysis.

The barium salt is extremely characteristic, separating from a claret-coloured solution in bright *orange*, silky needles, grouped together in wavy tufts. In order to prepare it, the substance was dissolved in a solution of baric hydrate, from which the excess of barium was precipitated at the boiling temperature by means of carbon dioxide. The solution was then concentrated to the crystallising point. As the evaporation proceeded, a film of the salt, in an amorphous condition, and of the *same* colour as the solution, formed at the edge of the liquid, on the evaporating basin. The salt is much more soluble in hot than in cold water. After recrystallisation, the orange needles gave the following figures on analysis :—

I.	0·2152 gram of substance gave	0·0744 $BaSO_4$.
II.	0·2883 ,, ,,	0·0987 ,,
III.	0·2478 ,, ,,	0·0854 ,,

	Found.			Calculated for	
	I.	II.	III.	$(C_{15}H_{15}O_4)_2Ba,H_2O$.	$(C_{15}H_{15}O_4)_2Ba$.
Ba (p. c.)..	20·32	20·12	20·26	20·35	20·91

The above figures were obtained from different preparations, dried over sulphuric acid, and also at 110°.

The salt evidently contains 1 mol. of water of crystallisation, although the attempts to determine this by loss were unsuccessful. Heated at 110° for several hours, no change in weight occurred, and decomposition commenced at somewhat higher temperatures. It was, however, observed that the orange crystals, when rubbed, became dark *magenta-red*, and analysis proved the altered salt, dried at 105—110°, to be anhydrous. Under the microscope, it showed no definite structure, and, when moistened with water, it immediately became *orange*, at the same time swelling up, and then passing into solution. On evaporation, the characteristic orange needles of the salt, as above described, were again obtained.

The anhydrous salt was prepared for analysis by thoroughly grinding the orange crystals, in small quantities at a time, in an agate mortar. The conversion was not easily accomplished, and it seemed as if a resinous substance were being dealt with. The powdered substance was heated at 110° until constant in weight.

I. 0·3368 gram of substance gave 0·1182 $BaSO_4$.
II. 0·2834 „ „ 0·1002 „

	Found.		Calculated for
	I.	II.	$(C_{15}H_{15}O_4)Ba$.
Ba	20·63	20·78 p. c.	20·91 p. c.

The two determinations were made with different preparations.

The calcium salt is entirely different from the barium salt just described. It separates from its solution on evaporation in small, dark-red crystals, and is only very sparingly soluble either in hot or in cold water. After drying over sulphuric acid, it did not lose in weight when exposed for over an hour to a temperature of 105—110°. Analysis shows it to be anhydrous.

I. 0·3113 gram of substance gave 0·0808 $CaSO_4$.
II. 0·2594 „ „ 0·0635 „

	Found.		Calculated for
	I.	II.	$(C_{15}H_{15}O_4)_2Ca$.
Ca......	7·63	7·19 p. c.	7·16 p. c.

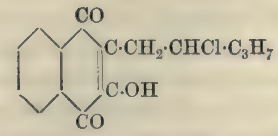
The preparations analysed were different: I was obtained by adding the theoretical quantity of calcium chloride to the slightly ammoniacal solution of the acid; on expelling the excess of ammonia by heat, the salt separated; II was prepared in the same manner as the above described orange variety of the barium salt.

The silver salt was obtained by precipitating a concentrated neutral solution of the ammonium salt with the calculated quantity of silver nitrate. It separates in a semi-resinous condition, becoming granular after some time. It is decidedly soluble in water, also in dilute alcohol, from which it separates, on spontaneous evaporation, in small, dark-red needles. The figures it gave on analysis lie between those required for $C_{15}H_{15}O_4Ag$ and $C_{15}H_{15}O_4Ag + H_2O$. It is probable, therefore, that the compound was not obtained in a pure condition.

Hydroxyhydrolapachol is readily dissolved by concentrated hydrochloric acid; the solution, however, becomes almost immediately turbid, and crystals of chlorhydrolapachol are formed. One gram of the finely powdered substance was added to 10 c.c. of hydrochloric acid, sp. gr. 1·10. The lumps which formed at first were thoroughly broken up with a glass rod. After 10 minutes, the temperature was raised to about 50°, and, 15 minutes from the time of mixing, the substance was thrown on to a funnel provided with a perforated platinum cone, and washed first with concentrated hydrochloric acid, and then with water. The heating must not be prolonged beyond the time given, or α-lapachone + xHCl (see p. 636) will crystallise out. Rather more than 50 per cent. of the substance operated on was thus obtained as pure chlorhydrolapachol, which, when once crystallised from alcohol, melted sharply at 113°. It will be shown subsequently (p. 637) that chlorhydrolapachol is also formed by the action of concentrated hydrochloric acid on β-lapachone; but as hydroxyhydrolapachol is much more readily converted into chlorhydrolapachol than β-lapachone, although the latter dissolves in the concentrated acid with great readiness, the conversion is undoubtedly brought about by the direct interchange of –OH for –Cl, and not by the formation of β-lapachone in the first stage of the reaction.

Concentrated sulphuric acid dissolves hydroxyhydrolapachol, forming an orange-red solution, from which water precipitates β-lapachone.

Chlorhydrolapachol,



This substance is formed (1) by the direct addition of hydrogen chloride to lapachol; (2) by the action of concentrated hydrochloric acid on hydroxyhydrolapachol; (3) by the action of the hydrochloric acid on β-lapachone. It is most conveniently prepared directly from lapachol.

Paternò and Caberti (*Gazzetta*, **21**, 379) have studied the action of hydrogen chloride on lapachol. They passed the dry gas through an acetic acid solution of lapachol in the cold, and obtained as a result a mixture of three substances, which they believed to be lapachone, unchanged lapachol, and the substance (α-lapachone) melting at 116—117°, which Paternò (*Gazzetta*, **12**, 371) had previously obtained in small quantity, by the action of concentrated nitric acid on lapachol. Of these three substances, the former was said to predominate, whilst the third-mentioned compound was present in traces only. The substances were not isolated, and were identified only by their appearance under the microscope.

I subsequently made a more thorough study of the action of hydrogen chloride with a view to the isolation of chlorhydrolapachol, the existence of which as an intermediate compound in the conversion of lapachol into lapachone, Paternò does not seem to have suspected. At the time that these experiments were made, the presence of the double bond in the amylene chain had not been demonstrated by the formation of a simple addition compound; the isolation of chlorhydrolapachol was of additional importance on this account.

After numerous trials, the following method of preparation was finally adopted:—

Twenty grams of lapachol are dissolved by the aid of heat in 300 c.c. of acetic acid. The solution is cooled to 50°, and 100 c.c. of concentrated hydrochloric acid, of sp. gr. 1·20, are then added. A precipitate, consisting of unchanged lapachol, is immediately formed, but this speedily redissolves, and crystals of chlorhydrolapachol are gradually deposited. The solution may now be completely cooled, and concentrated hydrochloric acid added at intervals, in small quantities, until 400 c.c. in all have been used. The larger portion of the acid is added to complete the precipitation of the chlorhydrolapachol, which is almost entirely insoluble in acetic acid containing large quantities of hydrochloric acid. It is added gradually, so that better developed crystals may be formed and the subsequent washing of the compound facilitated. As chlorhydrolapachol is, under these conditions, easily resolved into β-lapachone and hydrogen chloride, a considerable quantity of β-lapachone is invariably produced, even under the most favourable circumstances; this, however, remains entirely in solution, β-lapachone being very readily soluble in concentrated hydrochloric acid. The acid having been added, the crystals are thrown on to a funnel containing a plug of glass-wool resting on a platinum cone, and thoroughly washed with the aid of a pump, first with concentrated hydrochloric acid and then with water; the water must not, however, be used until all the mother liquor has been completely displaced, or otherwise β-lapachone will be precipitated. By following these directions, about 50 per cent. of the weight of the lapachol employed is obtained as chlorhydrolapachol in a very pure form.

As β-lapachone may, under suitable conditions, be converted into chlorhydrolapachol, it seemed desirable to demonstrate that in the method of preparation just described chlorhydrolapachol results from the direct addition of hydrogen chloride to lapachol, and that the latter is not first converted into β-lapachone. On substituting β-lapachone for lapachol and following the directions above given, no chlorhydrolapachol was obtained.

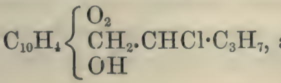
Chlorhydrolapachol was purified for analysis by crystallisation from alcohol; prolonged or unnecessary heating of the alcoholic solution should be avoided, as under such conditions hydrogen chloride is slowly liberated and α- and β-lapachone and other substances are formed. Chlorhydrolapachol usually separates from its alcoholic solution in small, crystalline plates which, when seen in contact with the mother liquor, strikingly resemble in form and external characteristics the crystals of lapachol. When dry, however, the compound lacks the golden tint which pure lapachol exhibits, being more of a canary yellow. In this form the compound undergoes a remarkable change when allowed to remain in contact with its saturated mother liquor; the crystalline plates gradually redissolve and are replaced by irregular bundles of flattened prisms, the change being usually complete in the course of 24 hours or so. Both forms of crystals have the same melting point, 113°. On analysis, the compound gave the following figures:—

I. 0·2489 gram of substance gave 0·5848 gram CO_2 and 0·1228 gram H_2O.

II. 0·2505 gram of substance gave 0·1276 gram AgCl.

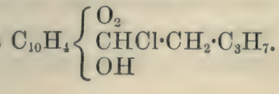
	Calculated for $C_{15}H_{15}O_3Cl$.	Found.	
		I.	II.
C........	64·63	64·07	—
H	5·38	5·48	—
Cl.......	12·74	—	12·59

If the formulæ of lapachol and hydroxyhydrolapachol have been correctly given in respect to the side chain, the behaviour of chlorhydrolapachol clearly indicates that it has the formula



$$C_{10}H_4\begin{cases}O_2\\CH_2.CHCl\cdot C_3H_7,\\OH\end{cases}$$

and not



$$C_{10}H_4\begin{cases}O_2\\CHCl\cdot CH_2\cdot C_3H_7.\\OH\end{cases}$$

Concentrated sulphuric acid dissolves chlorhydrolapachol, forming an intensely orange-red solution, with simultaneous evolution of hydrogen chloride. 0·7 gram was dissolved in 10 c.c. of concentrated sulphuric acid; the solution was allowed to stand 10 minutes, and then poured into a relatively large volume of water; an orange, crystalline precipitate, consisting of a neutral substance, was obtained. Although apparently pure, it did not fuse sharply until three times crystallised from alcohol. Its melting point was then 152—153°. The compound was, therefore, lapachone, which was further identified by conversion into hydroxyhydrolapachol, this, in turn, being recognised by its physical properties and its very characteristic orange barium salt.

Chlorhydrolapachol is slowly decomposed by prolonged heating with alcohol, but is far more readily decomposed on heating with acetic acid. The solution becomes perceptibly darker almost immediately, hydrogen chloride is evolved on boiling, and if the heating be continued for an hour or so, the addition of water produces an orange, crystalline precipitate which no longer reddens potassic hydrate. This precipitate consists of a mixture of two substances, α- and β-lapachone, the former resulting, as will be subsequently shown, from the action of the liberated hydrogen chloride on chlorhydrolapachol. It was found impossible to separate the two substances by fractional crystallisation, owing to the small quantity operated on and the great solubility of both compounds. Advantage was, however, taken of the fact that an alcoholic solution of β-lapachone very readily yields a sparingly soluble hydroxime, whilst α-lapachone, under the same conditions, remains unchanged. The mixed substances were dissolved in sufficient dilute alcohol to retain them in solution even after standing some time. An excess of hydroxylamine hydrochloride was then added and the solution warmed; golden needles of β-lapachone monohydroxime were soon deposited, which, when once crystallised from alcohol, fused sharply at 166—167°. The mother liquor from which the β-lapachone hydroxime was filtered off, was slightly diluted with water and allowed to stand for an hour or two; the precipitate, consisting of a mixture of β-lapachone monhydroxime and α-lapachone, was discarded. The solution was again diluted, this time considerably. The yellow crystals collected on the following morning, when once recrystallised from dilute alcohol, melted sharply at 114°, and resembled, in other respects, α-lapachone.

The behaviour of chlorhydrolapachol, in contact with dilute caustic alkalis is very instructive, as lapachol, hydroxyhydrolapachol, and α- and β-lapachone are simultaneously formed.

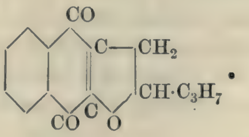
The formation of β-lapachone, a β-quinone derivative, from chlorhydrolapachol, unquestionably an α-quinone derivative, by the action of caustic alkalis, would seem to be an exception to the general rule previously referred to.

Chlorhydrolapachol dissolves readily in dilute caustic potash, giving an intensely red solution which is at first bright, but almost immediately becomes turbid, and rapidly deposits small, orange needles. 1 gram of the finely-powdered substance was treated with 140 c.c. of a cold, 1 per cent. solution of potassic hydrate, and the whole thoroughly stirred for a few minutes. The orange crystals were then collected, and, when dry, were found to be about half the weight of the chlorhydrolapachol taken. The mother liquor, which still remained intensely red, on being acidified with acetic acid, became turbid, and soon deposited a yellow, crystalline substance, which, when purified by recrystallisation from alcohol, melted at 134—137°, and otherwise resembled lapachol, giving its characteristic barium salt. The solution from which lapachol was filtered off was allowed to stand several days, when crystals of hydroxyhydrolapachol were found to have separated. This substance was recognised by its crystalline form, by its melting point, 124°, and by conversion into its barium salt, which, by loss of water of crystallisation, on slight friction changed from bright-orange to dark-red.

Attempts were made to purify the orange needles obtained from the alkaline solution as above described, by recrystallising them from alcohol, but, as after repeating the operation several times the melting point of the substance covered a wide range, a microscopic examination was made which revealed the presence of yellow needles. The two compounds were separated, as described above, by means of hydroxylamine hydrochloride, and β-lapachone monoxime and α-lapachone were obtained.

Concentrated hydrochloric acid in the cold appears to exert little or no action on chlorhydrolapachol, but when heated with it for a short time at about 100° in a sealed tube, a complete conversion into α-lapachone is effected. The same change takes place on dissolving the substance in acetic acid containing hydrogen chloride, and heating the solution for about an hour on a water-bath.

α-Lapachone,



α-Lapachone may be conveniently prepared as follows:—2 grams of lapachol are dissolved in a mixture of 20 c.c. of acetic acid and 5 c.c. of concentrated hydrochloric acid, sp. gr. 1·20, and the solution heated on a water-bath for one hour and a quarter; α-lapachone is then precipitated in a crystalline condition by the gradual addition of water to the acid solution. This precipitate, after being washed with water, is partially or completely dried, and redissolved in about 15 c.c. of acetic acid, to which 0·1 gram of chromic acid dissolved in a small quantity of water is added, for the purpose of destroying a trace of colouring matter which it is difficult to remove by crystallisation alone; the solution is then boiled for two or three minutes until quite green, and water is slowly added until the whole of the α-lapachone has crystallised out. α-Lapachone is thus obtained in a very pure condition. The yield is almost quantitative.

The mechanism of the change appears to be the following:—The lapachol is first converted into chlorhydrolapachol, which is then, for the most part, immediately changed into β-lapachone; at higher temperatures, the β-lapachone is slowly reconverted into chlorhydrolapachol, and from this α-lapachone is directly formed. Both β-lapachone and chlorhydrolapachol can be shown to be present in the solution in considerable quantities during the early stage of the change, so that, for the reason given, either of these substances can be substituted for lapachol in the preparation of α-lapachone.

The above method is extremely satisfactory, and succeeds equally well with large or small quantities. α-Lapachone may also be prepared by the following method, which gives almost quantitative results, and is as convenient as that described above.

Five grams of β-lapachone are dissolved in 150 c.c. of concentrated hydrochloric acid, sp. gr. 1·2; the flask containing the solution is loosely corked, and it is then immersed in warm water, the temperature of which is kept at 50° to 55°, for one hour, when it is gradually increased to 65°, and maintained at this point for about half an hour. The separation is then complete, and the solution is filled with yellow crystals consisting of an addition product of α-lapachone and hydrogen chloride; these are thrown on to a funnel containing a perforated platinum cone, and washed first with concentrated hydrochloric acid* and then with water. The addition compound is decomposed by the water, and α-lapachone is thus obtained in minute clusters of microscopic needles. The compound is then once crystallised from alcohol or dilute acetic acid.

Lapachol cannot be substituted for β-lapachone in the method just described, as it is not sufficiently soluble in concentrated hydrochloric acid, action taking place much more readily in a sealed tube at 70—80°.

If in the preparation of α-lapachone from β-lapachone a considerably smaller quantity of hydrochloric acid than that given above be used, chlorhydrolapachol will crystallise out in the course of a few minutes. Its existence as an intermediate product is thus demonstrated. The formation of chlorhydrolapachol from β-lapachone is theoretically important, and for this reason the conditions to be observed in obtaining it are given in detail below.

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* The use of hydrochloric acid for washing is precautionary, as, should there be any unchanged β-lapachone in the mother liquor, this would be precipitated by water, and thus render the α-lapachone impure.

Ten grams of finely-powdered β-lapachone are dissolved in 20 c.c. of concentrated hydrochloric acid, sp. gr. 1·20, and immediately after mixing, the solution is gently warmed by immersion in warm water, the temperature being kept at 48—52°; the β-lapachone dissolves very readily to an intensely orange-red solution, and in a few minutes crystalline leaflets begin to separate. When the heating has continued precisely 20 minutes from the moment of mixing, an additional 20 c.c. of concentrated hydrochloric acid is added, and the whole is immediately thrown on to a funnel provided with a platinum cone, and the hydrochloric acid mother liquor filtered off as rapidly as possible. Concentrated hydrochloric acid, in which chlorhydrolapachol is almost insoluble, is freely used to wash out all traces of the mother liquor; the acid is then in turn displaced by water. Rather more than 2 grams are thus obtained in a pure condition. The above directions must be carefully followed or a mixture of chlorhydrolapachol and α-lapachone will be obtained. The length of the time of heating is perhaps of the most importance, and should this be increased by two or three minutes, there will be considerable danger of obtaining an admixture of α-lapachone. The purity of the compound can be readily tested; it should leave no unchanged yellow particles after being moistened with dilute sodic hydrate, and the crystalline leaflets, subsequent to being thoroughly washed with hydrochloric acid, should remain unchanged on the addition of water. This observation should be made with the aid of the microscope.

In the course of some experiments on the oxidation of β-lapachone by dilute nitric acid, I have also observed the formation of α-lapachone. 1 gram of finely-powdered β-lapachone was suspended in 200 c.c. of dilute nitric acid, sp. gr. 1·045, the solution boiled for 40 minutes, and then rapidly cooled and filtered; α-lapachone separated from the filtrate, but the quantity did not exceed 6 to 7 per cent. of the weight of the β-lapachone employed.

The formation of α-lapachone in small quantity from lapachol by the action of concentrated nitric acid in the cold has already been recorded by Paternò (*Gazzetta*, **12**, 371).

The following analyses show that α-lapachone is isomeric with β-lapachone:—

0·1496 gram of substance gave 0·4062 CO_2 and 0·0787 H_2O

	Found.	Paternò found.	Calculated for $C_{15}H_{14}O_3$.
C........	74·05	74·16	74·38
H	5·84	5·87	5·78

The molecular weight of α-lapachone was found by Raoult's method to be 265; this figure represents the mean of two determinations, and agrees sufficiently closely with the formula $C_{15}H_{14}O_3$, which requires a molecular weight of 242.

α-Lapachone melts at 117°. It is readily soluble in most of the ordinary solvents, but only very slightly in water. It crystallises well from dilute acetic acid, and also from alcohol, being deposited as pale-yellow needles. It volatilises with difficulty with steam.

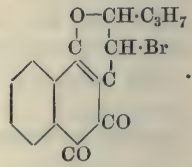
On distillation with zinc-dust, α-lapachone apparently yields the same products as lapachol (Paternò). Heated with acetic anhydride even in the presence of sodic acetate, α-lapachone does not appear to form any acetyl derivative; if sodic acetate is present, greenish, resinous substances are formed. My experiments were conducted at ordinary pressures.

Crystals of α-lapachone become opaque when immersed in concentrated hydrochloric acid, owing to the formation of an addition product. The opaque substance when examined under the microscope is found to be covered with minute crystals, which, on the addition of water, disappear, and are replaced by hair-like needles of α-lapachone. The addition compound also gives off hydrogen chloride when exposed to the air, or when immersed in concentrated sulphuric acid.

Concentrated sulphuric acid dissolves α-lapachone readily, and if water be added immediately, it is, in part at least, reprecipitated unchanged; if, however, the solution be allowed to stand for a few minutes, the α-lapachone is completely converted into β-lapachone.

α-Lapachone is insoluble in alkalis in the cold, but is gradually dissolved by a boiling 1 per cent. solution of sodic hydrate to an intensely coloured solution, somewhat of a claret-red. Acetic acid precipitates from this solution hydroxyhydrolapachol, which is obtained under similar circumstances from β-lapachone.

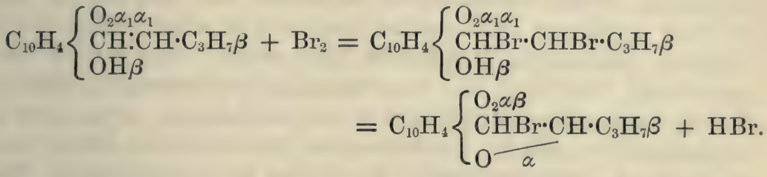
Bromo-β-lapachone (*Paternò's Bromolapachic Acid*),



Paternò obtained his so-called bromolapachic acid by the action of bromine on "lapachic acid" in acetic acid solution (*Gazzetta*, **12**, 353).

In the directions given by him for the preparation of the compound, stress is laid upon the necessity of adding the bromine to the lapachol as rapidly as possible, in order to obtain a good yield. With the constitution which Paternò assigned to bromlapachone, no reason suggests itself for the considerable difference in yield brought about by the slow or rapid addition of the bromine; but, nevertheless, the desirability of observing Paternò's instructions in this respect was confirmed by my own experiments. The same difference was also observed when chloroform was substituted for acetic acid. As soon as the bromlapachone formula suggested itself, the reactions involved became clearer, and the differences brought about by the variation in the method of adding the bromine could be then readily explained.

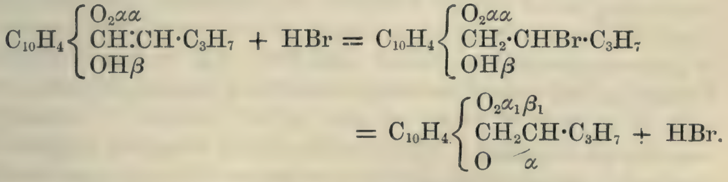
On the addition of bromine to lapachol, the following action first occurs :—



$$C_{10}H_4\left\{\begin{array}{l}O_2\alpha_1\alpha_1\\ CH{:}CH\cdot C_3H_7\beta\\ OH\beta\end{array}\right. + Br_2 = C_{10}H_4\left\{\begin{array}{l}O_2\alpha_1\alpha_1\\ CHBr\cdot CHBr\cdot C_3H_7\beta\\ OH\beta\end{array}\right.$$

$$= C_{10}H_4\left\{\begin{array}{l}O_2\alpha\beta\\ CHBr\cdot CH\cdot C_3H_7\beta\\ O\quad\alpha\end{array}\right. + HBr.$$

If the bromine is added slowly, the lapachol is in excess throughout the operation, and the hydrogen bromide which, as the equation indicates, is liberated, will form bromhydrolapachol, which in turn gives off hydrogen bromide, with the formation of β-lapachone.



$$C_{10}H_4\left\{\begin{array}{l}O_2\alpha\alpha\\ CH{:}CH\cdot C_3H_7\\ OH\beta\end{array}\right. + HBr = C_{10}H_4\left\{\begin{array}{l}O_2\alpha\alpha\\ CH_2\cdot CHBr\cdot C_3H_7\\ OH\beta\end{array}\right.$$

$$= C_{10}H_4\left\{\begin{array}{l}O_2\alpha_1\beta_1\\ CH_2CH\cdot C_3H_7\\ O\quad\alpha\end{array}\right. + HBr.$$

As the hydrogen bromide is thus regenerated, it is obvious that a very small quantity only is necessary to transform the whole of the lapachol into β-lapachone; and the extent to which this is effected will depend on the length of time given to the hydrogen bromide to act. Hence, the more slowly the addition of the bromine is brought about, the more β-lapachone, and consequently the less bromolapachone, will be obtained.

The conversion of lapachol into β-lapachone can be readily shown by passing dry hydrogen bromide gas through the chloroform solution of lapachol, but it is necessary to guard against an excess of hydrogen bromide, as β-lapachone may be readily changed by its action into other substances. The perfectly analogous action of hydrogen chloride has been already described, and in this case it was found possible to isolate the intermediate chlorhydrolapachol, which was subsequently converted into β-lapachone. From the above considerations, it is obvious that in order to reduce the formation of β-lapachone to a minimum, or to prevent it altogether, the bromine, and *not* the lapachol, should be in excess; hence it is desirable to add the lapachol to the bromine, and not bromine to the lapachol. Far better results were obtained after the importance of this was realised, and better results were thus obtained than by brominating in the presence of mercuric oxide.

The following method of preparing bromo-β-lapachone will be found to furnish a considerably larger yield of the compound than that given by Paternò. A solution of 30 grams of lapachol in 400 c.c. of chloroform is added at one operation to 22 grams of bromine in 200 c.c. of chloroform; both solutions should be ice-cold, and it is well to keep the flask containing the bromine immersed in water cooled by ice, until the whole of the lapachol has been added. The flask is then immediately transferred to a water-bath, and the chloroform distilled off completely; the distillation must not be delayed, or the yield of bromolapachone will be diminished; as the chloroform distils over, bromine and hydrogen bromide accompany the first portions. The residue, an orange oil, is dissolved in 75 c.c. of alcohol. In a short time bromo-β-lapachone commences to crystallise out, and after 12 hours or more it is filtered off, and washed with a little alcohol. From 25 to 26 grams are thus obtained in a very pure condition. The mother liquor and alcohol washings are evaporated to about 35 c.c., a crystal of bromo-β-lapachone is then added, and the solution covered to prevent evaporation, and set aside for a day or two to crystallise. From this, the bromo-β-lapachone separates in a dense crystalline mass, upon the surface of which compact yellow rosettes of dibromhydrolapachol are deposited. The crystals of the latter are scraped off as thoroughly as possible, and the partial mechanical separation thus effected renders easy the subsequent purification of the bromolapachone by crystallisation from alcohol. The total yield of bromo-β-lapachone is usually rather more than the weight of the lapachol operated on. It occasionally happens that a small quantity of dibromo-β-lapachone* is deposited from the mother liquor after evaporation, together with the other compounds. Dibromo-β-lapachone is readily distinguished by its physical properties; it is obtained under these conditions as microscopic needles of a light orange colour, which, owing to their slight solubility in alcohol, can be readily separated.

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* Mr. A. D. Gray has made a detailed study of the preparation and properties of this compound in my laboratory. The results obtained will shortly be published.

The bromolapachone was first carefully compared with that prepared as directed by Paternò, and in all particulars was found to be identical. A bromine estimation was made, with the following result:—

0·2588 gram of substance gave 0·1502 AgBr.

	Found.	Calculated for $C_{15}H_{13}BrO_3$.
Br	24·69	24·92

Bromolapachone has been observed by Paternò to separate from its solution in alcohol in orange-red, crystalline plates. While able to confirm this observation, the author has also obtained it, when in a pure condition, crystallised in tufts of fine needles, and the ease with which either form of crystal may be obtained is one of the most striking characteristics of this compound.

The conditions under which both varieties of crystals are formed may be stated generally as follows:—

From slightly impure alcoholic solutions, bromolapachone separates in plates, this being the case whether the solution is allowed to remain at perfect rest or be disturbed while crystallisation is proceeding. From pure concentrated solutions, bromolapachone can be readily obtained in plates by keeping the solution slightly in motion while the compound is crystallising out. If the compound, crystallised in plates and still in contact with its saturated mother liquor, be allowed to stand one or more weeks, the plates will be gradually replaced by tufts of needles. This change is believed to occur only when the compound is in a very pure condition. The observation was first accidentally made, and the experiment was then repeated several times.

Pure solutions protected from dust and allowed to stand absolutely at rest frequently deposit the compound crystallised entirely in tufts of needles. By observing only partially the above conditions, both varieties of crystals may often be obtained in the same solution. A saturated solution can be made to deposit the compound entirely in needles or plates by introducing the desired form of crystal to start crystallisation.

The above remarks apply to all alcoholic solutions of bromolapachone, whether obtained from needles or plates.

The melting points of the two varieties of crystals differ only very slightly, if at all. That of the plates was found to be 138·5°; that of the needles, 138°.

A combustion of the needles gave the following results:—

0·2399 gram of substance gave 0·4932 gram CO_2 and 0·0870 gram H_2O.

	Found.	Calculated for $C_{15}H_{13}BrO_3$.
C	56·06	56·07
H	4·02	4·04

Bromo-β-lapachone does not form an addition product with bromine, as it might be expected to do if it were in reality bromolapachol as suggested by Paternò. The author has allowed it to remain for several days in contact with the theoretical quantity of bromine in chloroform solution, but has not observed the formation of any addition compound. Bromolapachone was recovered unchanged.

Bromo-β-lapachone does, however, form unstable addition products with hydrogen chloride and bromide. In order to prepare the bromine compound, bromolapachone is immersed in concentrated aqueous hydrobromic acid, in which it dissolves readily. In the course of a few minutes the addition compound separates in orange needles. The compound may be washed with concentrated hydrobromic acid and dried on a porous plate, but it commences to decompose almost as soon as it is removed from the acid solution, giving off hydrogen bromide, and becoming reconverted into bromo-β-lapachone. The compound is immediately decomposed by contact with water. The chlorine compound is similar, but less easy to prepare, owing to bromo-β-lapachone being much less soluble in hydrochloric than in hydrobromic acid. The very instability of these compounds is sufficient evidence that they are not such as would be required to give support to Paternò's bromolapachol formula; nevertheless it is desirable that their existence should be recorded. The compounds were not analysed.

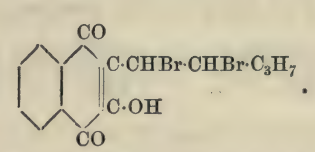
Bromo-β-lapachone is readily converted into lapachol by the action of zinc-dust in alkaline solution (compare Paternò and Caberti, *Gazzetta*, **21**, 374). This is best accomplished as follows:—To 1 gram of finely powdered bromo-β-lapachone small quantities of 10 per cent. sodic hydrate are gradually added, and the substance is simultaneously carefully mixed until the whole is thoroughly moistened and no longer repels the alkaline solution. The quantity of sodic hydrate used is then increased to 15 c.c., and 1 gram of zinc-dust is added. The solution is allowed to stand for about 40 minutes in a loosely corked flask, being slightly agitated at intervals, and is then diluted with about 100 c.c. of water. After the zinc-dust has completely separated, the solution is poured off, and air is drawn through it for an hour or two until thoroughly oxidised. It is then filtered and poured into an excess of dilute hydrochloric acid; lapachol separates entirely free from resin, and equal in quantity to at least 75 per cent. of the theoretical yield. This action, which is full of theoretical interest, has been already discussed in the opening pages of this paper.

Bromo-β-lapachone dissolves readily in a warm solution of acid sodic sulphite, from which colourless crystalline leaflets are deposited.

Orthotoluylenediamine and bromolapachone readily react in alcoholic solution: the azine obtained will be described in detail in a subsequent paper.

That the bromine of bromo-β-lapachone is not situated in the naphthalene nucleus is abundantly proved by the formation of phthalic acid on oxidation (Paternò), and further by the ease with which it is removed by dilute alkalis.

Dibromhydrolapachol,



The yellow substance obtained from the mother liquor in the preparation of bromolapachone (see p. 640), and still mixed with some of the latter, is purified by repeated recrystallisation.* The mixture is dissolved in a small quantity of alcohol, and crystallisation started by the addition of a crystal of bromolapachone or of the dibromo-compound, according as the one or the other of these is present in the larger quantity. It will be found possible by the successive introduction of crystals of the two substances into the same solution to obtain first the one compound and then the other, each in a comparatively pure condition. The mother liquor may then be concentrated by evaporation, and the crystallising operation repeated. After preliminary separation in this manner, no difficulty will be experienced in obtaining the substance quite pure by several recrystallisations from alcohol.

Dibromhydrolapachol as thus prepared forms yellow, crystalline plates closely resembling lapachol and chlorhydrolapachol in appearance. The crystals effloresce, however, on exposure to the air, and were found on analysis to contain alcohol of crystallisation. Only a small portion of the alcohol is lost at ordinary temperatures, and even prolonged exposure at 80° was found insufficient to completely expel it. At 100° the alcohol is all given off.

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* Dibromhydrolapachol cannot be separated from the admixed bromolapachone by extraction with sodic or potassic hydrate: even a very dilute solution of the alkali decomposes it with elimination of the bromine.

I. 0·8074 gram of substance heated to 100° until constant in weight lost 0·0291 gram.
II. 0·2403 gram gave 0·3988 gram CO_2 and 0·0855 gram H_2O.
III. 0·2332 „ 0·2084 „ AgBr.

	Calculated for $3C_{15}H_{14}Br_2O_3,C_2H_6O$.	Found.		
		I.	II.	III.
C_2H_6O	3·67	3·60	—	—
C	45·04	—	45·06	—
H	3·83	—	3·95	—
Br	38·33	—	—	38·02

The substance, heated at 100° until constant in weight, was also analysed with the following results:—

I. 0·2278 gram gave 0·3707 gram CO_2 and 0·0684 gram H_2O.
II. 0·2698 „ 0·2491 „ AgBr.

	Calculated for $C_{15}H_{14}Br_2O_3$.	Found.	
		I.	II.
C	44·77	44·38	—
H	3·48	3·33	—
Br	39·80	—	39·28

Finally, the substance, previously completely purified by crystallisation from alcohol, was dissolved in benzene, and after the addition of light petroleum, set aside to crystallise. It was thus obtained in plates, resembling those deposited from alcohol, but entirely free from alcohol, benzene, &c.

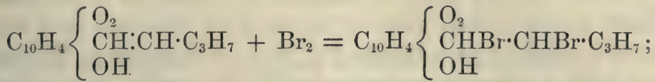
0·2307 gram of substance gave 0·3782 gram CO_2 and 0·0742 H_2O.

	Calculated for $C_{15}H_{14}Br_2O_3$.	Found.
C	44·77	44·70
H	3·48	3·57

Dibromhydrolapachol dissolves readily in boiling alcohol, benzene, chloroform, acetone, acetic acid, &c. The crystals deposited from acetic acid, like those from alcohol, effloresce on exposure to the air.

When crystallised from benzene and light petroleum, it melts at 132°; when containing alcohol of crystallisation, the melting point is slightly lower.

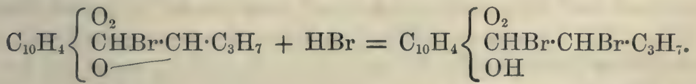
Dibromhydrolapachol is formed by the direct addition of bromine to lapachol, thus :—



$$C_{10}H_4\left\{\begin{matrix}O_2\\ CH{:}CH{\cdot}C_3H_7\\ OH\end{matrix}\right. + Br_2 = C_{10}H_4\left\{\begin{matrix}O_2\\ CHBr{\cdot}CHBr{\cdot}C_3H_7\\ OH\end{matrix}\right. ;$$

by far the greater part of the latter, however, is immediately converted into bromo-β-lapachone with elimination of hydrogen bromide.* This is all the more surprising, as, contrary to expectation, dibromhydrolapachol, in a pure condition, exhibits but a very slight tendency to pass into bromo-β-lapachone. It might at first be supposed that the hydrogen bromide or bromine present played some important part in bringing about this change; but dibromhydrolapachol has been proved by the experiments given below, to be perfectly stable in contact with these substances in chloroform solution, and hence it is difficult to explain why the transformation into bromo-β-lapachone occurs.

It is not impossible that the whole of the dibromhydrolapachol first formed may, under the conditions of the experiment, at the moment of formation, pass into bromolapachone; and later, the conditions having changed, that the bromolapachone may be in part reconverted by the hydrogen bromide present, into dibromhydrolapachol, thus :—



$$C_{10}H_4\left\{\begin{matrix}O_2\\ CHBr{\cdot}CH{\cdot}C_3H_7\\ O\text{———}\end{matrix}\right. + HBr = C_{10}H_4\left\{\begin{matrix}O_2\\ CHBr{\cdot}CHBr{\cdot}C_3H_7.\\ OH\end{matrix}\right.$$

Owing to the readiness with which hydrogen bromide attacks bromolapachone in chloroform solution, with the formation of a variety of products, I have not, so far, been able to obtain any conclusive experimental evidence in corroboration or refutation of this view; but there is an almost exact parallel in the case of chlorhydrolapachol, which can be obtained from, or converted into, β-lapachone, by the action of hydrochloric acid under varying conditions.

A small quantity was dissolved in chloroform, and hydrogen bromide passed through the solution, the light-yellow colour of which remained unchanged: there was no indication of the formation of bromo-β-lapachone.

The solution, saturated with hydrogen bromide, was still yellow, after standing 12 hours, and the residue left on the evaporation of the chloroform was completely soluble in dilute sodic hydrate, and hence contained no bromo-β-lapachone.

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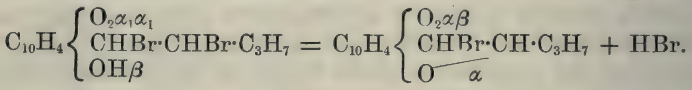
* Only about 3 per cent. of the lapachol used in the preparation of bromo-β-lapachone was obtained as dibromhydrolapachol. Many variations were made in the method of brominating without increasing the yield. The presence of mercuric oxide exerted no beneficial effect.

A solution of 0·33 gram of bromine in 10 c.c. of chloroform was gradually added to 0·83 gram of dibromhydrolapachol (the whole at that time available), also dissolved in 10 c.c. of chloroform. The solution was set aside to evaporate spontaneously; the residue once crystallised from alcohol was recognised as the unchanged substance by its melting point, by its solubility in dilute sodic hydrate, and other properties.

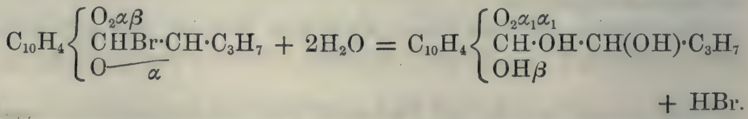
Concentrated sulphuric acid dissolves dibromhydrolapachol to an orange-red solution, and slowly converts it, with evolution of hydrogen bromide, into bromo-β-lapachone, thus :—



$$C_{10}H_4\left\{\begin{array}{l}O_2\alpha_1\alpha_1\\ CHBr\cdot CHBr\cdot C_3H_7\\ OH\beta\end{array}\right. = C_{10}H_4\left\{\begin{array}{l}O_2\alpha\beta\\ CHBr\cdot CH\cdot C_3H_7\\ O\overline{\qquad}\alpha\end{array}\right. + HBr.$$

0·5 gram was dissolved in 2 c.c. of concentrated sulphuric acid; the solution soon commenced to fume slightly, but the evolution of hydrogen bromide was not sufficiently rapid to cause the formation and escape of bubbles of the gas. Soon after the compound had completely dissolved, the sulphuric acid solution was poured into about 100 c.c. of water. An orange-coloured precipitate formed, which collected into a lump, and soon hardened; this proved to be the unchanged substance, accompanied by a small quantity of an orange compound, and when once crystallised from alcohol it melted sharply at 130—131°. It was redissolved in about the same quantity of concentrated sulphuric acid, and this time allowed to stand 16 hours; when poured into water, an orange precipitate was formed, which became crystalline on standing. Crystallised from alcohol, the compound was found to be no longer soluble in sodic hydrate; it was orange in colour, and was recognised by its melting point and other properties to be bromo-β-lapachone, crystallising like this compound in the two characteristic forms described above.

The action of dilute alkalis on dibromhydrolapachol is interesting, as it gives additional evidence of the relation existing between it and bromo-β-lapachone. It will be shown in the following pages that boiling aqueous alkalis convert bromo-β-lapachone into dihydroxyhydrolapachol, as indicated in the following equation :—



$$C_{10}H_4\left\{\begin{array}{l}O_2\alpha\beta\\ CHBr\cdot CH\cdot C_3H_7\\ O\overline{\qquad}\alpha\end{array}\right. + 2H_2O = C_{10}H_4\left\{\begin{array}{l}O_2\alpha_1\alpha_1\\ CH\cdot OH\cdot CH(OH)\cdot C_3H_7\\ OH\beta\end{array}\right. + HBr.$$

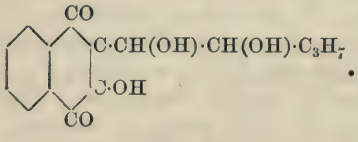
Similarly, dihydroxyhydrolapachol is also formed by the action of alkalis on dibromhydrolapachol.

$$C_{10}H_4\left\{\begin{array}{l}O_2\alpha\alpha\\ CHBr{\cdot}CHBr{\cdot}C_3H_7\\ OH\beta\end{array}\right. + 2H_2O = C_{10}H_4\left\{\begin{array}{l}O_2\alpha_1\alpha_1\\ CH(OH){\cdot}CH(OH){\cdot}C_3H_7\\ OH\beta\end{array}\right.$$
$$+ 2HBr.$$

One gram of the finely powdered substance was immersed in 50 c.c. of a 1 per cent. solution of sodic hydrate; it dissolved readily, giving an intensely red solution, which, although at first bright, became turbid after a few minutes from the separation of a very small quantity of an orange-red substance, which was filtered off shortly afterwards. The alkaline filtrate was then allowed to stand about 12 hours, during which time a slight additional deposit of a greenish colour was formed. The solution, once more filtered, was acidified with acetic acid, and a compound was thus obtained, on standing, having all the properties of dihydroxyhydrolapachol. When crystallised from alcohol, it still contained slight traces of bromine, and was, therefore, once more dissolved in dilute sodic hydrate and reprecipitated. After crystallisation from acetic acid, all traces of bromine had disappeared, and the compound proved to be pure dihydroxyhydrolapachol.

It is an interesting fact that, while dibromhydrolapachol dissolves with great readiness in dilute caustic soda, it is but slowly dissolved by a moderately concentrated solution.

Dihydroxyhydrolapachol,



This compound is formed by the action of caustic alkalis on bromo-β-lapachone, or on hydroxy-β-lapachone, and also on dibromhydrolapachol. It is best prepared as follows:—12 grams of finely powdered bromolapachone and 900 c.c. of a 1 per cent. solution of caustic soda are boiled together with a reflux condenser. The bromolapachone dissolves slowly to an intense carmine-red solution. At the end of 15 minutes the boiling is discontinued and the solution filtered. Stray crystals of bromolapachone which have escaped grinding and are consequently able to resist the action of the potash for a long time, are thus removed; a small quantity of a green substance, formed by the action of the soda, is also retained on the filter paper. A slight excess of acetic acid is added to the filtered solution when cold, resulting in the immediate formation of a precipitate in small quantity, consisting of a brownish substance. This is removed as quickly as possible by filtration through a folded paper of comparatively large size. The filtration must be promptly accomplished, otherwise the substance will commence to crystallise out before the separation of the brown impurity has been effected. In a very few minutes after acidifying, the dihydroxy-derivative commences to be deposited from the now orange-red solution in compact, yellow, crystalline grains. The separation occurs slowly, the solution becoming simultaneously lighter in colour. In the course of 24 hours the crystallisation, which can be considerably promoted by vigorous stirring, is complete, and the compound can be collected, washed well with water, and dried. The compound, as thus obtained, is almost pure:* 12 grams of bromolapachone give rather more than 8 grams of the new product. It can be obtained pure by one crystallisation from acetic acid. For analysis it was crystallised from alcohol, in which it is not very soluble. A qualitative test showed that the bromine had been removed.

0·1867 gram gave 0·4442 CO_2 + 0·0989 H_2O.

	Found.	Calculated for $C_{15}H_{16}O_5$.
C	64·88	65·21
H	5·88	5·79

Dihydroxyhydrolapachol melts at 181—182°. Like bromolapachone, it crystallises from 95 per cent. alcohol in two apparently different forms. No special experiments were made to determine the conditions governing the formation of each variety of crystal, and sometimes the one form, sometimes the other, would be obtained under apparently similar conditions. One modification (that analysed) consists of small, prismatic crystals, often grouped together in the form of compact stars; the other, of very fine, long needles, crystallising in tufts.

Like hydroxyhydrolapachol and lapachol, it forms stable metallic derivatives which are not decomposed by carbon dioxide. The colour of their solutions is similar to that of those of lapachol. The strontia compound is the only one of those examined which can be readily obtained in a crystalline form. It consists of very small, dark-red needles. The lime, barium, and silver compounds were obtained as amorphous films only.

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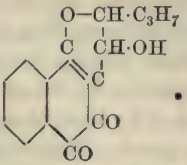
* If the crude substance be dissolved in a very slight excess of 1 per cent. sodic hydrate and immediately filtered, orange crystals consisting of Savernò's isolapachone will be retained on the filter-paper. This substance was most carefully identified by its fusing point and by a variety of reactions as yet unpublished, which Mr. Shepard has found to be characteristic of the compound prepared as described by Paternò.

The action of concentrated sulphuric acid on dihydroxyhydrolapachol is being studied at the present time in my laboratory. Some interesting results have been obtained.

Concentrated hydrochloric acid dissolves dihydroxyhydrolapachol slowly, simultaneously converting it into hydroxy-β-lapachone,

Hydroxy-β-lapachone,



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Hydroxy-β-lapachone is readily formed by the action of dilute mineral acids on dihydroxyhydrolapachol. The compound was prepared for analysis as follows:—

To a solution of 1·36 grams in the smallest possible quantity of boiling 95 per cent. alcohol, 5 c.c. of concentrated hydrochloric acid were added: the colour of the solution changed to an intense orange-red. After boiling for one or two minutes, the solution was diluted with water as long as a precipitate was produced; in this way a considerable portion of the hydroxylapachone was obtained in small, orange-red needles. The filtrate, still orange in colour, was evaporated until a crust of crystals had formed upon its surface, and these were separated from the solution when cool. Total yield, 1·15 grams. The substance, on being purified by crystallisation from dilute alcohol, separated in red needles, melting at 201·5°, and closely resembling β-lapachone in appearance.

0·2507 gram gave 0·6401 CO_2 + 0·1228 H_2O.

	Found.	Calculated for $C_{15}H_{14}O_4$.
C.............	69·63	69·76
H.............	5·44	5·42

Although the above method of preparing hydroxy-β-lapachone is entirely satisfactory in operating with small quantities, it is not so well adapted to the preparation of the compound on a larger scale, owing to the comparatively large volume of alcohol needed to dissolve the dihydroxyhydrolapachol.

The following method, which was subsequently discovered, will be found generally far more convenient, and is probably equally well adapted to the preparation of the compound in large or small quantities. 2 grams of finely powdered dihydroxyhydrolapachol were immersed in 5 c.c. of concentrated hydrochloric acid, sp. gr. 1·20.

After standing in a corked flask for about an hour, the compound was found to have completely dissolved. The acid solution was then poured into about 100 c.c. of water, when hydroxy-β-lapachone separated in a very pure form. Yield, 1·72 grams. The filtrate and aqueous washings were evaporated on a water-bath, and a further yield of about 0·08 gram was obtained, making in all 1·80 grams. The yield is therefore theoretical, the calculated figures being 1·86.

Hydroxy-β-lapachone, like β-lapachone and bromo-β-lapachone, is almost insoluble in alkalis in the cold; on boiling, however, it readily passes into solution. 35 c.c. of 1 per cent. solution of caustic potash and 1·35 grams of hydroxylapachone were heated for several minutes at the boiling point. The solution was then filtered, cooled, and acidified with acetic acid. Crystals commenced to form almost immediately, but the separation was not complete for some hours. After crystallisation from alcohol, the compound melted at 181—182°, and in other respects was found to be identical with dihydroxyhydrolapachol obtained as above described from bromolapachone. The yield of the substance was almost theoretical; 1·35 grams gave 1·36 grams of the dihydroxy-derivative, 1·45 being required by theory.

0·1834 gram gave 0·4390 CO_2 + 0·0958 H_2O.

	Found.	Calculated for $C_{15}H_{16}O_5$.
C	65·28	65·21
H	5·80	5·79

LVIII.—*The Atomic Weight of Boron.*

By J. L. Hoskyns Abrahall, B.A. (Oxon.), Ph.D. (Munich), late Bishop Berkeley Fellow of the Owens College, Manchester. (Edited by T. Ewan and P. J. Hartog, of the Owens College.)

Preface.

[The work recorded in the following memoir was carried out by the author during the years 1889–91 in Professor Dixon's laboratory at the Owens College. It was brought to an end by his untimely death in October, 1891*.

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* See obituary notice, in the *Manchester Guardian*, Oct. 17th, 1891, and in this Journal, Trans., 1892, p. 486.

This memoir has been drawn up mainly from the contents of five rough note-books, which contain the actual record of the author's experiments as they were performed in the laboratory. But certain missing particulars, with regard to the preparation and titrations, the editors have been obliged to fill in from their own knowledge; whilst for others they are indebted to Messrs. Harden, Ormandy, and Stanton, whom they here desire to thank. The atomic weights had in most cases only been calculated approximately from the observations; for the application of corrections, and for the calculations of which the results are now given, the editors are responsible. They feel deeply how much more imperfect must be the present exposition of the research than that which the author would have given; but, as they were better acquainted with its details than any other of his friends, they undertook the task of editing it.

It may be added that a considerable number of bulbs filled with the various fractions of boron bromide, which served for the last series of determinations, have been preserved. These were intended for additional experiments. The editors hope that, before long, this material may be utilised.—T. E., P. J. H.]

Historical Introduction.

The element boron was isolated almost simultaneously by Davy (*Phil. Trans.*, 1808, i, 43) and by Gay-Lussac and Thénard (*Annales de Chimie*, **68**, 169 and *Recherches Physico-chimiques*, 1811, i, 308), who found, by oxidising boron with nitric acid, that the sesquioxide contains about one-third of its weight of oxygen. This number would give 48 as the atomic weight of boron. Almost at the same time, H. Davy (*Phil. Trans.*, 1809, i, 82) also obtained free boron, and found, by burning it in oxygen, that the oxide was composed of 1 part of boron and 1·8 parts of oxygen, from which number the atomic weight of boron is calculated to be 13·3. The first accurate determination of the atomic weight is due to Berzelius (*Ann. Phys. Chem.*, 1824, **2**, 128), who estimated the amount of water of crystallisation in borax. The borax was first fused in order to destroy organic matter, and then recrystallised and dried between sheets of filter-paper for 24 hours, after which it was powdered and exposed to the air for varying lengths of time in order to get rid of mechanically enclosed water. A weighed quantity of the substance was heated carefully in a platinum crucible until it finally melted at a red heat. Three experiments which gave identical results showed that the percentage of water in borax is 47·1.[*] The atomic weight recalculated from this number[†] is B = 11·059.

In 1849 (*Compt. rend.*, **29**, 7; and *J. pr. Chem.*, **47**, 415), Laurent published a further determination of the water of crystallisation of borax. He found that on throwing a piece of iron into melted borax, hydrogen was evolved, and concluded that the whole of the water was not driven off from this salt by simple fusion. He therefore mixed it with about one-tenth of its weight of powdered Iceland spar, and thus obtained the numbers 47·15 and 47·20 for the percentage of water. He did not, however, regard his experiments as very exact. The atomic weights recalculated from these results[†] are 10·978 and 10·857; mean = 10·917.

Finally, in 1859, Dumas (*Ann. Chim. Phys.* [3], **55**, 181, 1859) included in his well-known memoir on atomic weights the record of three experiments made by Deville, in which boron chloride and boron bromide were precipitated with silver. The atomic weights recalculated from Deville's experiments[†] are as follows:—

(*a*) from BCl_3	10·808
(*b*) from BBr_3	10·964

The discrepancies between the results obtained by previous observers led the author to undertake a redetermination of the atomic weight in question. For this purpose, he performed three series of experiments, depending on (1) the estimation of the water of crystallisation in borax, and (2) the estimation of the amount of silver necessary to precipitate the bromine of a given weight of boron bromide (preliminary and final series).

Determination of the Water of Crystallisation in Borax, $Na_2B_4O_7,10H_2O$.

The borax used was recrystallised once slowly, and twice suddenly, from a supersaturated solution in ordinary distilled water, and, finally, a fourth time from a supersaturated solution in redistilled water. The small crystals thus obtained were freed from the mother liquor by means of the water-pump, and allowed to stand in a vacuum of 5 mm. over anhydrous borax for a week.

Owing to the fact that on heating crystallised borax in the air it swells up to an enormous extent, it was found extremely difficult to drive off the water in this way without incurring mechanical loss of the substance. The following process of dehydration was, therefore, used. The borax was weighed in a platinum crucible, and this was supported on a pipeclay triangle, and slipped into a wide glass tube, sealed up at one end (AB, Fig. 1). A lump of quicklime was then introduced into the tube, and the end closed with a well-fitting india-rubber stopper, through which passed a tube connected with a closed manometer, D, and, further, at E with a water-pump capable of reducing the pressure to the vapour tension of water. The end of the glass tube AB, in which the platinum crucible stood, was placed in an air-bath made from a biscuit tin. The crucible was thus heated in various experiments for very different lengths of time (5—20 hours) to between 250° and 300°; but practically the whole of the water that could be expelled at this temperature was found to come off in the first three or four hours. About $\frac{1}{2}$ per cent. of water still remained in the substance after the longest continued heating. To remove this residual quantity of water, the crucible was taken out of the tube and heated over the naked flame of a Bunsen burner until the weight became approximately constant; in some cases the final heating was done with a blowpipe.

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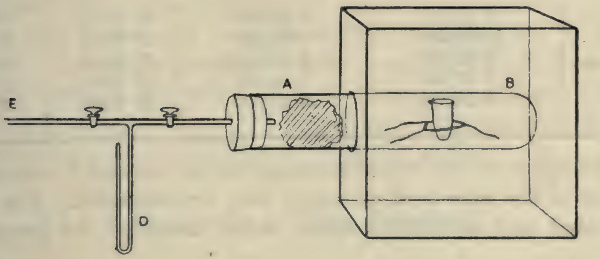
[*] The weights seem only to have been determined to the centigram.

[†] In the following memoir, we have used throughout the following atomic weights: O = 16, Na = 23·051, Ag = 107·923, Br = 79·951, the numbers calculated by Clarke (*Constants of Nature*). We have taken H = 1·0077, this number being the mean of the numbers given by Stas (1·0075), Cooke and Richards (1·0083), Noyes (1·0072), Rayleigh (1·0069), and Dittmar and Henderson (1·0085). (See Ramsay in the *Year-book of Science* for 1891, p. 132.)—T. E., P. J. H.

FIG. 1.



The experiments recorded below were only considered by the author as preliminary, and were carried out in order to determine under what conditions they must be performed to be sufficiently accurate for atomic weight determinations.

The following experiment shows that no boracic acid or other substance is volatilised with the water of crystallisation at 265° in a vacuum. A certain quantity of borax was introduced into a tube, a plug of asbestos was then inserted, the tube exhausted, and all the water which came over on heating was condensed and collected. It did not act on turmeric paper, and left no appreciable residue when left to evaporate in the cold over sulphuric acid.

It was, however, found on heating melted borax over a blowpipe that the flame was coloured yellow, which seems to show that it volatilises, at least to some minute extent, at high temperatures.

It was observed that on prolonged heating over a Bunsen burner the weight of the crucible and contents, which diminished at first, finally began to increase. This final increase may have been due to absorption of sulphur from the flame.

The following are the results of these preliminary experiments, of which the data are sufficiently complete to allow of an atomic weight being calculated from them:—

No. of expt.	Corrected weight of $Na_2B_4O_7 + 10H_2O$.	Corrected weight of residual $Na_2B_4O_7$.	Percentage of H_2O, found.	Atomic weight of B.
A 85.......	7·00667	3·69587	47·2069	10·843
A 91.......	12·95936	6·82560	47·3308	10·593
A 113	4·65812	2·45248	47·3504	10·554
A 129	7·47208	3·93956	47·2763	10·703
A 131	4·94504	2·60759	47·2686	10·719

The numbers of the experiments given in Column 1 correspond to the pages of the note-book on which they are recorded. The weights of hydrated and anhydrous borax were corrected for buoyancy in air.

As has already been said, the weight of the fused borax in some cases reached a minimum value, after which it increased. This minimum value (corresponding to the highest percentage of water) has in these cases been taken as the final weight of the fused borax. The weighings (performed by the method of vibrations) were probably accurate to $\frac{1}{10}$ milligram. They have been corrected for errors in the weights used and for buoyancy in air. [For a full account of the application of these corrections see p. 661.] As the fourth place of decimals is probably correct in the actual weighings, the fifth place has been preserved in the corrected numbers.

The following remarks on the single determinations may be of value:—In A 91 and A 113, the borax was finally heated in a small Fletcher furnace capable of melting cast iron easily. In both cases the temperature was, therefore, exceptionally high, and the loss exceptionally great; the atomic weight calculated from the result is therefore low. A 129 and A 131 were the two last experiments made, and are probably more worthy of confidence than the preceding ones. In A 131, the borax was finally fused over the blowpipe. The actual weighings in a given instance are quoted to show the variations which occur on prolonged heating.

Crucible + borax fused with Bunsen burner....	27·30345
re-fused ,, ...	27·30462
,, blowpipe............	27·30312
,, for half an hour	27·30253

The determination of the atomic weight of boron by this method necessitates the determination of the precise range of temperature within which all the water of crystallisation of borax can be driven off, while none of the anhydrous substance is volatilised. That this is no easy matter, the above experiments clearly show. In spite of their apparent concordance,* therefore, Berzelius's results cannot be finally accepted as trustworthy.

[The method is evidently open to objection on another score, namely, that it is exceedingly rare to find bodies which crystallise with an exact number of molecules of water of crystallisation. On the one hand, the mother liquor may be included mechanically; on the other hand, the salt may be slightly deliquescent or slightly efflorescent. It is quite possible† that the compound $Na_2B_4O_7 + 10H_2O$ may yield some of its water of crystallisation to anhydrous borax, both bodies tending to form a lower hydrate with a lower tension of dissociation than the decahydrate.—T. E., P. J. H.].

Preparation of Boron Bromide.

a. Preparation of Boron.—The method followed was that described by Wöhler and Deville. A considerable amount of trouble was taken in attempting to purify the borax completely. Pure boracic acid (of commerce) was first boiled with a small quantity of baryta to free it from sulphuric acid, which adheres to it very tenaciously, and was then recrystallised in small portions at one time. The boracic acid so obtained was fused over the blowpipe in a platinum dish, and poured out on to an iron plate, broken up and powdered, and passed through a sieve.

The powdered substance was then heated in an iron crucible with sodium, under a layer of sodium chloride, exactly in the way described by Wöhler and Deville (*Ann. Chim. Phys.* [3], **52**, 63, 1858). The mass was poured into hydrochloric acid and filtered, and the boron mud thus obtained was transferred to a platinum dish and treated with strong hydrochloric acid and ammonium fluoride (to remove iron and silica), the liquid being warmed. It was finally washed with alcohol and hydrochloric acid, and alcohol and ether, and dried in a vacuum. It appears that this preparation was not pure, but still contained iron

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* See note *, p. 652.

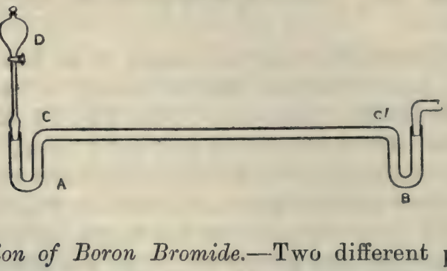
† This suggestion is due to Dr. Harden.

(perhaps in the form of a boride?). A second preparation of boron was made, the fused mass being poured, as before, into hydrochloric acid and then washed by decantation till free from the acid. As soon as this is the case, the boron begins partly to dissolve, partly to suspend itself in the water, and from these washings, boron free from iron was obtained, by precipitating with hydrochloric acid, re-suspending by treatment with potash, and precipitating again with hydrochloric acid. The boron thus freed from iron was then dried on a porous tile in a vacuum for a month. It was found that it was impossible, however, to free it from water in this way, for on heating it in a vacuum at 100°, water, and at a higher temperature, hydrogen, were given off.

To free the boron from water and from any oxide which might be formed in the presence of water, a portion of it was washed with alcohol and then with ether, but on heating subsequently to this operation, hydrocarbons were evolved, and the attempt to obtain boron free from oxide was therefore abandoned, and it was decided to eliminate the products due to its presence at a later stage.

b. Preparation of the Bromine.—The editors can find no details with regard to the bromine used in Preparation 1 (*infra*). The bromine used in Preparation 2 was made in the following way:—A solution of potassium bromide was treated with bromine and shaken up with pure carbon bisulphide to free it from iodine. The bromide was then crystallised and heated with pure potassium dichromate and dilute sulphuric acid, and the bromine thus obtained was finally distilled over pure, red-hot, electrolytic copper to free it from chlorine. [It is possible that other precautions to ensure its purity were also taken. —T. E., P. J. H.] It was collected in a stoppered funnel, D, Fig. 2, ground to fit the apparatus for the production of boron bromide.

Fig. 2.



c. Preparation of Boron Bromide.—Two different preparations of boron bromide were made from the boron obtained in the way described above. In the first, only 6 grams of boron were used, and the details given in the author's note-books are incomplete. This preparation was used for the preliminary set of determinations.

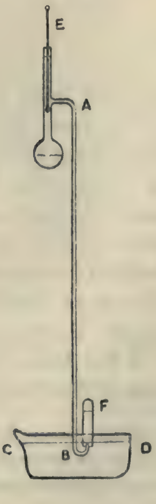
The second preparation was on a large scale, and the editors are able, from their own knowledge, to give somewhat fuller details with regard to it, although no notes on the subject have been preserved.

Preparation 1.—Six grams of boron were first ignited in hydrogen in a hard-glass tube placed in an ordinary combustion furnace, to free it from moisture; bromine was then distilled backwards and forwards over the substance heated to redness, the product allowed to stand over mercury till the excess of bromine was absorbed, and then distilled off from the mercuric bromide formed.

Preparation 2.—The apparatus used consisted of a hard-glass combustion tube, CC′, Fig. 2, about 1200 mm. in length, to the ends of which were fused the U-tubes A and B. The stoppered funnel D, containing the bromine, was ground to fit into the tube A, and the joint well wrapped round with lead foil. The bent neck of the distilling flask E which contained mercury was similarly ground into the U-tube B.

Bromine was slowly distilled over the red-hot boron placed between C and C′, and the bromide formed, together with the excess of bromine, were finally transferred to the distilling flask. This was then sealed up and the mixture allowed to remain in it until the colour of the bromine had disappeared. The substance was then redistilled into a clean dry flask of the form shown in Fig. 3, and from this flask it was finally distilled into the tube F, from which

Fig. 3.



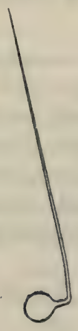
it was transferred to the glass bulbs used in the atomic weight determinations.*

The tube AB was about 1 metre long, so that when the flask was exhausted by means of the Sprengel pump, the mercury in the trough CD did not rush back into the flask. A thermometer, E, was sealed into the neck of the flask by wrapping it tightly round with thin lead foil, which, for further security, was enveloped outside with sheet india-rubber coated with coaguline.

The apparatus being so arranged, the boron bromide was distilled in fractions of 10 to 15 c.c. at a time into the test-tube F standing in the trough CD over dry clean mercury.

The separate portions of boron bromide were then introduced into thin glass bulbs of the form shown in Fig. 4, which had been previously weighed. In order to fill each bulb, it was first filled completely with the mercury. The open end of the capillary neck was then slipped up into the boron bromide at the top of the tube F, and by alternately warming and cooling the bulb with a small flame, the whole of the mercury was replaced by boron bromide. The capillary was then sealed off as close to the bulb as possible, and the neck was preserved along with the bulb to be weighed again.

Fig. 4.



The bulbs thus prepared always contained a small bubble of gas; this, however, consisted only of the vapour of boron bromide, as on slightly warming the bulb in the hand the bubble could be made to disappear entirely. The size of the bubbles varies rapidly with the temperature, so that boron bromide would appear to have a large coefficient of expansion.*

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* As the boron was not anhydrous, some hydrobromic acid must have been formed during the operation, but it is probable that by the action of the mercury and the mercuric bromide, and the repeated distillation of the boron bromide, it was finally completely eliminated.

Preparation of the Silver.

The silver used was prepared in various ways:—

(*a*) Was obtained as chemically pure from Schuchardt.

(*b*) Was prepared by reducing silver nitrate with ammonium sulphite in the presence of copper, according to the method described by Stas.

(*c*) Was made by reducing silver chloride with milk sugar, but the method used differed somewhat from that of Stas, and is therefore described. About 60 grams of recrystallised silver nitrate were fused till a small quantity of silver had been reduced; the melt was dis-

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* *Density of Boron Bromide.*—In order to apply the buoyancy correction to the weights of boron bromide, it was necessary to know the density of the liquid. This was determined (by the editors) with one of the bulbs (6) prepared by the author. The diameter of the bubble of boron bromide vapour resting against the side of the bulb at the temperature of the experiment (16·5°) was found to be 3·3 millimetres: its volume was known to be greater than a hemisphere, and less than a sphere. As the difference between the limiting values is a small quantity compared to the others which entered into the calculation, no sensible error was committed by supposing the mean to be the true value.

The density of the boron bromide was found from the following equation:—

$$d_B = \frac{B}{V - \frac{g}{d_g} - v},$$

where d_B = density of boron bromide.

B = weight of boron bromide (corrected for buoyancy by assuming the density to be that given by previous observers, that is, 2·7) = 10·8151 grams. This weight was determined as the difference of the weights of the bulb filled and empty. Strictly speaking, the weight of boron bromide vapour in the bubble should be subtracted from this number, but this weight cannot be more than $\frac{1}{1000}$ milligram, and is therefore negligible.

V = the volume of the filled bulb, known by a determination of its loss of weight in water of known temperature = 4·37381 c.c.

g = weight of glass of the bulb = 0·56388 gram.

d_g = density of the glass of the bulb = 2·4679.

v = volume of the bubble = 0·0137 c.c.

Whence we find—

$$d_B \text{ (at } 16·5°) = 2·6175.$$

Wöhler and Deville gave the number 2·69, but they do not state the temperature at which the determination was made, and which was probably 0°.

The result given above is of course affected by the uncertainty as to the exact volume of the bubble, but the limiting error in the density cannot amount to $\frac{1}{300}$ of the total value. As the density was only required to correct the weighings, greater accuracy was not attempted.—T. E., P. J. H.

solved in 250 c.c. of water, filtered, and the solution diluted up to 3 or 4 litres. It was then precipitated by means of pure, dilute hydrochloric acid, and the silver chloride formed was washed by decantation, and digested with aqua regia in the cold. It was then again washed and dissolved in 1 litre of water, saturated with ammonia, and filtered. 100 grams of twice recrystallised milk sugar were dissolved in 1 litre of water, and filtered into the silver solution. The mixture was allowed to stand for a day in the cold, then warmed, and finally boiled. The reduced silver was washed by decantation, first with cold water, and then with boiling water. The water used had been carefully redistilled from an iron can provided with a block-tin condenser. The silver obtained by the method described is in an extremely finely divided form, and the washing was very tedious. It was collected and melted on lime in the oxy-coal-gas blowpipe, care being taken to use an excess of oxygen. The silver used in the final set of determinations was then purified by electrolysis in the following way. Part of it was dissolved in nitric acid, and the solution of silver nitrate was placed in a platinum dish which formed the negative pole. The positive pole consisted of the remaining portion of the silver suspended in a linen bag, and connected to the battery by a platinum wire. The bag was hung from the top of a bell-jar which protected the solution from dust. A tangent galvanometer was included in the circuit, and the current regulated to the strength which was found by Lord Rayleigh and Mrs. Sidgwick (*Phil. Trans.*, ii, 1884, 411) to give the best results with the silver voltameter. Black crystals (of peroxide?) were formed in very small quantity, which grew in long, hair-like filaments, and sometimes reached from the dish across to the bag. They were, however, isolated, and easily removed (the silver, on melting in a vacuum, gave off no oxygen). The metal obtained was granular and brilliantly white.

The electrolytic silver was placed in a boat cut from a block of quicklime, and melted in a porcelain tube in a vacuum.

Weighings.

The weighings were all performed with a Ladd and Oertling balance provided with an optical arrangement for estimating accurately the amplitude of the swings of the pointer. [The balance has been described by Wills, Trans., 1879, **35**, 707.] All weighings were made by Gauss' method. The object to be weighed was first placed on the left-hand pan, four sets of vibrations (each consisting of 5 or 7 swings past the centre of the scale) were taken, and the position of the zero was calculated. This operation was repeated with the object to be weighed in the right-hand pan, and finally again with the object in the left-hand pan. The difference between the two weighings with the object on the left-hand pan never amounted to more than $\frac{1}{20}$ milligram, and generally was less than $\frac{1}{40}$. The mean of the two weighings with the object in the left-hand pan was of course in all cases taken. The difference between them was due to a slow change of the zero point which was found to be continuous throughout the series of operations. Such variation did not therefore introduce a sensible error into the weighing.

The temperature of the air in the balance case, and the barometric pressure were noted for each weighing. The air was assumed to be dry, as fresh calcium chloride was kept in the case.

The errors of the weights were determined three times in the course of the work, before each prolonged set of weighings. As two of the 1-gram weights happened to be precisely equal in weight, they were taken as standards.

The only weights for which the corrections varied more than one or two hundredths of a milligram were the 10-gram weight and the 5-gram weight. The correction for the 10-gram weight varied 0·6 milligram, and that for the 5-gram weight 0·3 milligram, during the three years over which the work extended.

The weighings of boron bromide (A) and of silver (B) were corrected for buoyancy in air by the following formulæ:—

(A.) Corrected weight of BBr_3 =

$$W - w + \sigma\left[\frac{W - w}{2{\cdot}617} - \frac{W_B - w_B}{8{\cdot}28} - \frac{W_p - w_p}{21{\cdot}23}\right],$$

(B.) Corrected weight of Ag =

$$W + \sigma\left[\frac{W}{10{\cdot}5} - \frac{W_B}{8{\cdot}28} - \frac{W_p}{21{\cdot}23}\right],$$

where W is, in A, the apparent weight in grams of the bulb full of boron bromide in air, and in B the apparent weight of silver in air.

w is the apparent weight of the glass bulb in air.

σ is the weight of 1 c.c. of air at the temperature and pressure noted during the weighing.

W_B and w_B are the brass weights used in making up the weights W and w.

W_p and w_p are the platinum weights used in making up the weights W and w.

[The correction for the rider is negligible.]

2·617 is the density of boron bromide.

8·28 is the density of the brass weights.

21·23 is the density of platinum (Everett).
10·5 is the density of silver.

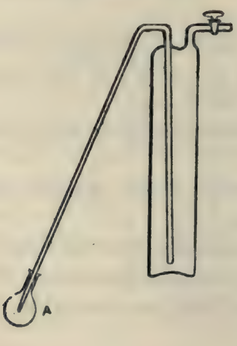
The density of the brass weights was determined by weighing the 50-gram weight in water. The error introduced by the difference between the actual density of the platinum weights used and the average of the numbers given in Everett's *C.G.S. Units*, which has been taken, could not introduce a sensible error into the experiments.

Titration of Boron Bromide.

When the weight of boron bromide in the bulb chosen for an experiment had been determined, a lump of silver was cut off from the mass, and reduced very nearly to the proper amount by means of a sharp, hard-steel chisel. It was next washed with dilute hydrochloric acid, ammonia, and water, and heated before the final weighing. It was then dissolved in nitric acid in a stoppered bottle. The bottle had walls about $\frac{1}{4}$ inch thick, and the stopper was ground in with care. When the silver was all dissolved, the bulb of boron bromide was introduced, the stopper inserted, and the bottle shaken so as to break the bulb. The sudden pressure, due to the evolution of gaseous hydrogen bromide, which did not immediately dissolve, was so great as to burst the bottle in some cases, a number of determinations being thus lost. Some bottles specially made for the purpose were used in the final determinations, of which one or two alone proved satisfactory.

The titrations were carried out by a method which in its essentials is that of Stas. A solution of silver nitrate was made up so that 1 gram of solution contained exactly 1·09 milligram of silver, and a potassium bromide solution was prepared which was exactly equivalent to it (by weight). These solutions were introduced into pipettes of the form shown in Fig. 5. The small glass cap A was ground on

FIG. 5.



to the end of the siphon tube, so as to prevent loss of liquid when the pipette was not in use. The pipettes were weighed (to the milligram) before and after each addition of solution.

The bottle was placed in a wooden box, blackened internally, and could be illuminated by the rays of a lamp, which were spread out into a flat pencil by means of a glass cylinder, placed with its axis horizontal. The slightest turbidity in the liquid could thus be detected after the addition of silver or bromide solution. Before repeating the addition of either solution, it was found advantageous to filter the supernatant liquid through a small filter into a test-glass, leaving the curdy mass of silver bromide at the bottom of the bottle. The filtered liquid was then poured back into the bottle, and tested afresh with bromide or silver solution, as the case might be. Towards the end of the reaction, a considerable time was allowed to elapse between the successive additions of these solutions; often only two or three drops were added in a day, so that each titration required a week or more for its completion.

It is well known that some excess of one (say, the silver) solution may be added before an additional drop ceases to produce a visible cloud; and after this point has been reached, a not inconsiderable amount of the other (say, the bromide) solution must be added before an additional drop of this solution ceases to produce a cloud. The silver solution was therefore first added, until the no-turbidity point was attained; the process was repeated with the bromide solution, and again with each solution alternately several times. It was assumed that half of the bromide solution added after silver had ceased to produce a visible reaction was equivalent to the excess of silver present at the beginning of this operation, and that the other half was itself present at the end of the operation as excess. Then, on adding the silver solution again, half the amount added was regarded as equivalent to the excess of bromide in the liquid, while the second half as before remained in excess at the end of the operation. In this way, the excess existing at the previous stage could be calculated from each addition of bromide or silver solution after the first. The mean of all the numbers thus obtained was taken to be the true excess present after the first addition of silver or bromide solution. In this way, the exact weight of silver necessary to precipitate the bromine in a known weight of boron bromide could be determined.

The atomic weight of boron was calculated from the experimental numbers by the formula

$$B = 3AgX - 3Br,$$

where B, Ag, and Br are the atomic weights of boron, silver, and bromine respectively, and X is the ratio of the weight of boron bromide taken to the weight of silver necessary to precipitate the bromine it contains.

Ag was taken = 107·923, Br = 79·951 (see note †, p. 652).

The following table gives the experimental data and atomic weights calculated from them:—

TABLE II.*—*Preliminary Series of Determinations.*

Fraction.	No. of bulb.	Weight of boron bromide.	Weight of silver weighed out.	Deficiency or excess determined by titration.	Total silver.	Ratio X = boron bromide / silver.	Atomic weight of boron.
—	10	1·31203	2·84299 −1·15058	+0·00165	1·69406	0·774489	10·902
—	7	4·39944	5·67589	+0·00240	5·67829	0·774783	10·998
—	4	5·04022	6·50785	+0·00035	6·50820	0·774441	10·887
—	1	6·51597	8·38890	+0·00029	8·38919	0·774326	10·850
—	9	7·75343	10·01369	−0·00134	10·01235	0·774388	10·870

It must be borne in mind that a given percentage error in the determination of X will produce a relative error 23 times as great in the value of B, a result which may easily be deduced from the equation given above, B = 323·769X − 239·853, if we replace X by its value 0·774. The author was, of course, aware of this, but the method described was chosen, nevertheless, as the most accurate one available.

The close agreement of determinations made with the various fractions of boron bromide of preparation ii (Table III) affords strong evidence that the substance was in a state of all but absolute purity. It must, however, be noticed that—

(1.) The pairs of experiments made with the same fractions, namely, 23 and 25, and 32 and 34, yield results which differ only by the 1/60,000th part of their value, and that this may probably be considered as the experimental error to which determinations made with the same fraction were liable.

(2.) The two results deduced from experiments made with the first fraction differ in a relatively marked way from the other five results.

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[*] The editors hesitated to insert this table, as the numbers are without comparison less concordant and trustworthy than those of Table III, but have decided to do so for the sake of completeness.

They have purposely omitted to calculate a mean atomic weight from the observations, as the author regarded them as purely preliminary.

TABLE III.—*Final Series of Determinations with Boron Bromide.*

Fraction.	Number of bulb.	Weight of boron bromide.	Weight of silver weighed out.	Deficiency or excess of silver determined by titration.	Total silver.	Ratio X $= \frac{\text{boron bromide}}{\text{silver}}$.	B = atomic weight of boron.
i	23	4·467835	5·769480	+0·001788	5·771268	0·774152	10·794
i	25	8·423151	10·880752	−0·000104	10·880648	0·774148	10·792
ii	19	1·655111	2·136486	+0·001107	2·137593	0·774288	10·838
iii	10	8·032352	10·373182	+0·001019	10·374201	0·774262	10·829
vi	32	4·092743	5·286621	−0·000672	5·285949	0·774268	10·831
vi	34	2·389993	3·086793	+0·000049	3·086842	0·774254	10·826
xi (?)	11	7·721944	9·974278	−0·000224	9·974054	0·774203	10·811

Mean of all the determinations. 10·817
Mean error .... ±0·016
Probable error.............. ±0·0047

Atomic weight determined from the ratio of the total quantity of boron bromide to the total quantity of silver employed in all the determinations = 10·812.

Mean of the last 5 determinations (excluding those made with the first fraction) .... 10·827
Mean error.................... ±0·007
Probable error .... ±0·003

Atomic weight determined from the ratio of the total quantity of boron bromide to the total quantity of silver employed in the last 5 determinations = 10·823.

(3.) Boron chloride has a lower boiling point than boron bromide, and if any of this substance were present as an impurity in the bromide, the major portion of it would distil over with the first fraction, and the atomic weight calculated from the determinations made with this fraction would, therefore, be too low.

Hence it would seem preferable to neglect the first two results, and to consider as the atomic weight yielded by these determinations the number calculated from the last five results.

The number thus obtained, B = 10·825, is, it will be seen, lower than that given by previous observers, and, moreover, differs considerably from the nearest whole number.

LIX.—CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

Mercuric Zinc Cyanide; a Study of the Mode of Formation and Properties of an Insoluble Double Salt.

By Wyndham R. Dunstan.

In a paper communicated to the Pharmaceutical Society in 1890 (*J. Pharm.* [3], **20**, 653; this Journal, Abstr., 1890, 855), I gave an account of the composition and properties of the white precipitate, resulting from the interaction of aqueous solutions of mercuric potassium cyanide and zinc sulphate, which was first observed by Rammelsberg [*Ann. Chim. Phys.* (Pogg.), **42**, 131], and described by him in connection with the properties of the mercuric potassium cyanide he had then discovered. In recording this reaction, Gmelin (*Handbook*, **7**, 424; **8**, 24) mentions that the same precipitate may be obtained by adding mercuric chloride to a solution of zinc potassium cyanide, $ZnK_2(CN)_4$, and since no hydrogen cyanide is produced, he suggests that double decomposition has occurred, and that the precipitate consists of mercuric zinc cyanide, $HgZn(CN)_4$. This suggestion has been accepted by subsequent writers, the reaction being expressed by the equations—

$$HgK_2(CN)_4 + ZnSO_4 = HgZn(CN)_4 + K_2SO_4;$$
$$ZnK_2(CN)_4 + HgCl_2 = HgZn(CN)_4 + 2KCl.$$

It does not appear, however, that the precipitate was ever analysed.

In his search for a satisfactory antiseptic surgical dressing, Sir

Joseph Lister, after having found neither zinc cyanide nor mercuric cyanide free from objection, determined to examine the effect of the double cyanide of zinc and mercury described by Gmelin. Its action, as an antiseptic material, was found to be superior to that of any substance previously tried, having none of the corrosive properties of mercuric cyanide, whilst acting more efficiently as an antiseptic than zinc cyanide.

In the preparation of the substance on a somewhat large scale, it was observed that the greater part of the mercuric cyanide was dissolved by the water used in washing the precipitate, and that only a small proportion remained in the precipitate, which consisted chiefly of zinc cyanide. This fact, combined with the circumstance that the amount of mercuric salt retained in the precipitate was subject to variation, led to the suspicion that the substance might be a mixture of the two cyanides.

It was found, however, that an intimate mixture of the two salts did not act antiseptically in the same manner as the precipitate, since the mercuric cyanide was readily dissolved from the mixture, and exerted a corrosive effect.

The question as to the nature of the precipitate was eventually referred by Sir Joseph Lister to the present writer, who undertook to investigate it. The enquiry has led to the observation of a number of facts of considerable chemical interest, and goes to show that, in many respects, the precipitate is a remarkable substance.

Preparation of Pure Materials.

The potassium cyanide used in these experiments was prepared by passing the vapour of hydrogen cyanide into an alcoholic solution of pure potash. The crystalline precipitate was collected, washed with alcohol, and dried in a vacuum on a porous tile. Potassium cyanide thus prepared is, of course, free from cyanate, and will not contain any appreciable quantity of carbonate if the alcoholic potash used in its manufacture has been freshly prepared.

The mercuric potassium cyanide, $HgK_2(CN)_4$, is prepared by dissolving finely powdered mercuric cyanide in a warm, concentrated, aqueous solution of potassium cyanide, containing rather more than the calculated amount of the salt. On evaporating the liquid, the double salt is deposited in crystals, which are once recrystallised from water. This compound is stable. If pure mercuric cyanide be not available, the double cyanide may be prepared by dissolving the calculated quantity of mercuric sulphate, in small portions at a time, in a slight excess of an aqueous solution of potassium cyanide. Mercuric chloride cannot be conveniently substituted for the sulphate in this process, since a double salt containing chloride is also formed, from which the mercuric potassium cyanide cannot be completely separated by recrystallisation. In many instances, when both pure potassium and mercuric cyanides have been at hand, the aqueous solution of the double cyanide required for the experiment has been prepared by dissolving the proper quantity of mercuric cyanide in the solution of potassium cyanide.

When zinc cyanide was required, it was obtained by precipitating a solution of zinc acetate with aqueous hydrogen cyanide. The double cyanide of zinc and potassium, $ZnK_2(CN)_4$, may be readily prepared by dissolving freshly precipitated zinc cyanide in a slight excess of aqueous potassium cyanide, or even more readily by adding aqueous potassium cyanide to a solution of zinc acetate until the precipitate at first formed is redissolved. The salt may be obtained pure by recrystallisation from water. If zinc sulphate is used instead of the acetate, considerable difficulty is experienced in completely separating the potassium sulphate.

Both mercuric potassium cyanide and zinc potassium cyanide are readily soluble in water, whilst zinc cyanide is insoluble. Mercuric cyanide, as is well known, is sparingly soluble in cold water.

Methods of Analysis.

The methods used in analysing the various products have not been exceptional in any important respect, and, therefore, only call for brief notice. The mercury, as a rule, has been estimated by heating the material with excess of lime in a combustion tube, and collecting the distilled mercury in the usual manner. When the amount of material was too small to admit of distillation of the metal, it has been estimated as sulphide. The zinc has been estimated by igniting a known weight of the substance at a low red heat until a constant weight of zinc oxide remained, a few drops of nitric acid being added when necessary, in order to facilitate the oxidation of the last traces of carbonaceous matter. Sometimes, when only a small quantity of material was available, and both zinc and mercury were to be estimated, the zinc, after removal of the mercury as sulphide, was precipitated with sodium carbonate and weighed as oxide. The correct determination of the amount of cyanide in the material was not at first found to be easy, for the reason that mercuric cyanide is very difficult to decompose. The direct conversion of the whole of the cyanogen into silver cyanide by heating the substance with dilute nitric acid and silver nitrate gave results which were much too low even when the operation was conducted in a closed tube at 100—120°. Ebullition with strong aqueous sodium carbonate, except after prolonged action, failed to afford the whole of the cyanogen in the form of sodium cyanide, especially when the material was rich in mercuric salt. This appears to be due to the combination of the sodium cyanide with mercuric cyanide to form the double salt, which is not readily decomposed by sodium carbonate.

Perfectly satisfactory determinations of the cyanogen were furnished by bringing the substance in contact with a mixture of zinc and dilute sulphuric acid from which hydrogen is being evolved, and conducting the resulting hydrogen cyanide into a solution of silver nitrate; the silver cyanide was collected and weighed. The indirect estimation of the cyanogen through the nitrogen, which was determined by Dumas' method, or through the ammonia obtained by the soda-lime method, also gave accurate results which agreed well with those furnished by the action of hydrogen. As a rule, it was most convenient to estimate the nitrogen by Dumas' method, the operation being conducted in a vacuum and the nitrogen collected through the limb of a Sprengel pump.

Formation and Composition of the Precipitate.

The first experiments were made to ascertain whether the composition of the precipitate, prepared by either of the two methods described by Gmelin, corresponds with the formula of the double salt $HgZn(CN)_4$ which he considers is probably formed.

A solution of mercuric potassium cyanide was precipitated with a solution of zinc sulphate, the quantities used being calculated from the equation $HgK_2(CN)_4 + ZnSO_4 = HgZn(CN)_4 + K_2SO_4$. The precipitation was carried out in the following manner. Mercuric cyanide (12·5 grams) was dissolved in about 60 c.c. of water and mixed with 40 c.c. of a solution containing rather more than the calculated quantity of potassium cyanide. This solution of mercuric potassium cyanide was precipitated by the addition of the calculated amount of zinc sulphate dissolved in about 60 c.c. of water. The copious white precipitate was collected and washed with cold water (about 50 c.c.) until no more soluble mercuric salt could be detected in the washings by means of hydrogen sulphide. The precipitate was then dried at 100°. Its bulk had been very considerably reduced in washing. The calculated quantity of the hypothetical double compound producible from these quantities of the reacting salts is 18·5 grams; the amount actually obtained was rather more than 2 grams. On analysis, the substance was found to have the following composition:—

Zinc cyanide.........	94	per cent.
Mercuric cyanide.....	6·7	,,

The substance also contained a small quantity of oxygen, estimated by ignition in a current of hydrogen, which appeared to be present as hydroxide of zinc. The amount of mercuric cyanide found is about one-tenth of that demanded by the formula $HgZn(CN)_4$, which requires 68·29 per cent.

In another experiment, the same quantities of salts were used, but less water was employed in dissolving them. The precipitate was washed with cold water until free from mercuric salt. The yield of precipitate was larger than in the former experiment, and it contained more mercuric cyanide, namely, 17·7 per cent.

This quantity of mercuric salt is rather more than one-fourth of that required by the formula $HgZn(CN)_4$.

These experiments were repeated, varying the quantities of the reacting salts and of the water used to dissolve them, but in no instance could the double salts consisting of equimolecular proportions of the two cyanides be prepared.

The second method which, according to Gmelin, probably furnishes this double cyanide was now tried. Zinc potassium cyanide (7 grams) was dissolved in water and the strong solution precipitated with 8 grams of mercuric chloride dissolved in water so that the following reaction might occur:—

$$ZnK_2(CN)_4 + HgCl_2 = ZnHg(CN)_4 + 2KCl.$$

The white precipitate was washed with cold water until free from soluble mercuric salt, then dried and analysed. It contained 9·67 per cent. of mercuric cyanide, the remainder being zinc cyanide with a little hydroxide. This quantity of mercuric salt corresponds with about one-seventh of that calculated from the formula $HgZn(CN)_4$.

It is therefore evident that the white precipitate which Gmelin thought to be the equimolecular double cyanide of zinc and mercury is a compound or mixture containing much less mercuric cyanide than this double salt.

Attempts were now made to prepare this double cyanide by other methods. A solution was made containing equivalent quantities of zinc potassium cyanide and mercuric potassium cyanide. This was decomposed with exactly sufficient dilute sulphuric acid to convert the potassium of both salts into sulphate; zinc cyanide and mercuric cyanide would then be set free in the proper proportion to form the hypothetical double salt,

$$ZnK_2(CN)_4 + HgK_2(CN)_4 + 2H_2SO_4 = ZnHg(CN)_4 + 2K_2SO_4.$$

The precipitate was collected, washed free from soluble mercuric salt, and dried. It contained 8·46 per cent. of mercuric cyanide, the rest being zinc cyanide. This quantity of mercuric salt is about one-eighth of that demanded by the formula $HgZn(CN)_4$.

Lastly, a fourth method was tried in order to prepare the double salt. Equivalent quantities of mercuric oxide and zinc carbonate, both freshly precipitated, were dissolved in a slight excess of a saturated aqueous solution of hydrogen cyanide:—

$$HgO + ZnCO_3 + 4HCN = HgZn(CN)_4 + CO_2 + H_2O.$$

Reaction immediately occurred, and a white precipitate gradually settled. After shaking and standing for some time in a closed bottle, the precipitate was collected, washed, dried, and analysed. It consisted almost entirely of zinc cyanide, and contained only a trace of mercuric salt.

It is proved by these experiments that the white precipitate obtained under the various conditions above described is principally composed of zinc cyanide, containing a variable quantity of mercuric cyanide, and is not the equimolecular double salt, as Gmelin suggested might be the case.

The properties of the precipitate were now examined, and further experiments were made in order to determine whether the mercuric cyanide is mixed with the cyanide of zinc, or if any evidence could be obtained of the existence of a chemical compound of the two cyanides.

Properties of the Precipitate.

Although the precipitate contains a variable quantity of mercuric cyanide, and in many respects resembles a mixture of the two salts, yet it presents some features of chemical interest. In the experiments of which an account has just been given, the amount of water present during precipitation was in every instance sufficient to dissolve only a small proportion of the mercuric cyanide produced. Nearly the whole of this salt is therefore precipitated with the insoluble cyanide of zinc. When the precipitate is washed with cold water, a large part of the mercuric salt is removed. It is, however, remarkable that although water, in a sufficient quantity of which mercuric cyanide dissolves without difficulty, should fail to extract the whole of the salt from the precipitate; a variable quantity, usually between 5 and 10 per cent., remains after the washings have ceased to react with hydrogen or ammonium sulphide. In what condition is this mercuric cyanide, which is so incorporated with zinc cyanide as to be insoluble in cold water?

The ability of cold water to completely dissolve mercuric cyanide from a mixture of it with zinc cyanide was demonstrated by washing an intimate mixture of these cyanides with cold water, when the whole of the mercuric salt passed into the filtrate, and left pure zinc cyanide on the filter. A specimen of the substance containing about 15 per cent. of mercuric cyanide was microscopically examined. It appeared to be a homogeneous, amorphous powder free from any crystalline particles.

Although the mercuric cyanide is not dissolved from the substance by washing with cold water, it is slowly removed by the action of boiling water. It was observed that if the precipitate is washed free from mercuric salt, and then dried at 100°, a small quantity of mercuric salt, usually from 2 to 3 per cent., can be dissolved from the dried substance by cold water. If this washed material is again dried at 100°, a further quantity of mercuric cyanide may be dissolved from it by cold water, and if the operation is repeated sufficiently often, the whole of the mercuric cyanide may be removed. The following results illustrate the course of this action. The material used had been washed free from mercuric cyanide and dried at 100°. A portion of it was then analysed, and the remainder washed and again dried. This series of operations was performed four times with the following results:—

After the first operation ..	12·0	per cent.	of mercuric	cyanide.
,, second ,, ..	10·46	,,	,,	,,
,, third ,, ..	9·09	,,	,,	,,
,, fourth ,, ..	8·26	,,	,,	,,

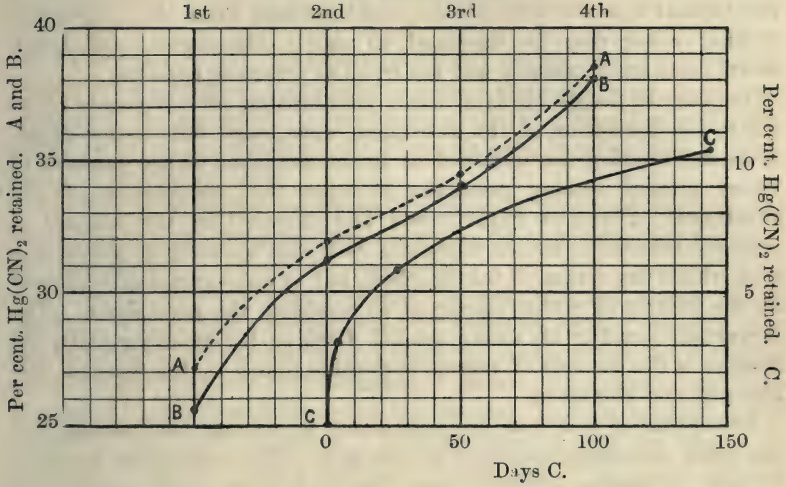
The residue was finally boiled with water for some hours, when the remainder of the mercuric salt went into solution.

That the liberation of the mercuric cyanide is due to the action of hot water on the substance, and not alone to the rise in temperature, was proved by drying some of the washed precipitate in a vacuous desiccator over calcium chloride, and then heating it for some hours at 100°. Cold water dissolved no mercuric salt from the substance which had been dried in this manner.

Further experiments as to the action of cold water (13—15°) on the substance have shown that, although it fails to dissolve the mercuric salt under the ordinary conditions of washing, when the water is in contact with the substance for only a short time, by prolonged contact with cold water the mercuric salt slowly passes into solution, although at a diminishing rate. This gradual action is shown in the curve, Fig. 1, C, which has been plotted from the results of an experiment which lasted 172 days; the amount of mercuric cyanide dissolved being determined from time to time.

FIG. 1.

¼ mol. $ZnSO_4$ added. A and B.



Action of Cold Water (Fig. 1, C).

Days.	Per cent. of $Hg(CN)_2$ removed.
3	3·15
26	5·73
143	10·42

The aqueous liquid, on evaporation, deposited crystals which were proved by analysis to be mercuric cyanide. The residue left undissolved by the boiling water consisted of zinc cyanide and hydroxide, the hydroxide being the result of the hydrolysis which occurs when zinc cyanide is boiled with water.

Nature of the Precipitate.

Two suggestions may be made with reference to the condition of the mercuric cyanide in the precipitate.

1. The mercuric cyanide may be combined with the zinc cyanide in the form of a double salt decomposable by water.

2. The mercuric cyanide may be entangled and mechanically retained by the cyanide of zinc. In the precipitation the two cyanides are thrown out together, and since there is not sufficient water present to dissolve the whole of the mercuric cyanide, there must be particles of this salt intermingling with those of the zinc cyanide which are aggregating to form the precipitate. Under these circumstances it is conceivable that a certain number of particles of mercuric cyanide

may become encased by the insoluble zinc cyanide, and thus be protected from the solvent action of cold water, which would never come into actual contact with them, except perhaps after long digestion. Boiling water may be supposed to slowly disintegrate and break down these small masses, and set free the mercuric cyanide.

In order to decide between these possibilities, several points relating to the formation of the substance were more fully investigated. More information was obtained as to the influence of the quantity of water present during precipitation upon the composition of the substance. Previous experiments had shown that the amount of retained mercuric cyanide fluctuates with the quantity of water present whilst the action is taking place, but is not appreciably affected by the volume of water employed in washing the precipitate. The larger the quantity of water used to dissolve the reacting salts, the smaller is the amount of mercuric cyanide found in the washed precipitate, and *vice versâ.*

Precipitation was now brought about by mixing very strong, but not quite saturated, solutions of the salts. The calculated quantity of pure potassium cyanide was dissolved in a small quantity of water, and the proper amount of finely powdered mercuric cyanide was dissolved in the warm liquid. The solution of mercuric potassium cyanide thus prepared was precipitated when cold by the addition of a concentrated solution of the equivalent quantity of zinc sulphate. The precipitate was collected and washed with cold water until all the soluble mercuric salt had been removed. It was then dried in a vacuum over calcium chloride, and analysed. The results were as follows:—

Mercuric cyanide......	36·17 per cent.
Zinc cyanide..........	64·0 ,,

Experiments made later, which are alluded to subsequently, have proved that by reducing the amount of water used in dissolving the salt to a minimum, the percentage of mercuric cyanide may be raised about 2·5 per cent. above this amount. On the other hand, by gradually increasing the volume of this water, specimens of material may be prepared containing any percentage of mercuric cyanide from about 38 per cent. to less than 1 per cent.

Striking as these results are, they do not enable us to decide between the chemical and physical explanations referred to above, for although they may be attributed to the gradual decomposition of a double salt by water, they are also susceptible of a physical explanation, since the more water there is present to dissolve the mercuric cyanide the smaller would be the proportion encased by the zinc cyanide.

If zinc cyanide combines with mercuric cyanide to form a double salt, which is readily decomposed by water, it seems possible that this salt might be formed under other circumstances than precipitation. An attempt was made to produce the compound by evaporating to dryness at 100° a mixture of freshly precipitated zinc cyanide with a strong aqueous solution of mercuric cyanide. The dried mass contained 10 per cent. of mercuric cyanide. Washing with cold water removed the whole of the mercuric salt, proving that no combination had taken place.

In other experiments an intimate mixture of the two cyanides was heated to various temperatures between 90° and 150°, but no combination occurred between the two salts.

Again, if the substance produced by precipitation contained an ordinary double salt decomposable by water, it seemed possible that this salt might be obtained in an almost pure state if the two cyanides were brought together in the absence of water. Equivalent quantities of freshly precipitated mercuric oxide and zinc carbonate* were suspended in a small quantity of absolute alcohol and the vapour of hydrogen cyanide passed into the mixture until the whole of the yellow mercuric oxide had disappeared and carbon dioxide had ceased to be evolved. On filtering the liquid and washing the precipitate with cold water, the mercuric cyanide was completely dissolved, and a residue of zinc cyanide remained. The conditions under which this experiment was made seemed to be most favourable to the formation of a compound of the two cyanides, but none was produced. So far, the facts might appear to lead to a physical rather than to a chemical explanation of the retention of the mercuric cyanide in the substance. When opportunity is afforded, as it is in precipitation, for the entanglement or encasement of mercuric cyanide by zinc cyanide to occur, the substance is formed. When the conditions are unfavourable to this action, but are, nevertheless, still conducive to chemical combination, as they are in the experiment just described, the substance is not produced. For these reasons, I suggested, in my former paper on the subject, that the phenomenon is probably physical and not chemical.

Further inquiries into the circumstances attending the formation and decomposition of the substance have, however, conclusively proved that the attachment of the mercuric cyanide to the zinc cyanide must be ascribed to chemical combination, which, however, does not occur to any appreciable extent when the two ready-made salts are brought together.

If the zinc cyanide entangles the undissolved mercuric cyanide during precipitation, and the action is purely mechanical and independent of any chemical attraction between the molecules, it ought to be found that other salts, whose solubility is about the same as that of mercuric cyanide, should also be entangled when precipitated together with zinc cyanide in presence of insufficient water for their solution. Potassium sulphate appeared to be a very suitable salt to employ in this crucial experiment, since its solubility is nearly the same as that of mercuric cyanide; 100 parts of water at the ordinary temperature dissolve 12 parts of mercuric cyanide and 11 parts of potassium sulphate.

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* The oxide was not used owing to the difficulty there is in preparing it pure by precipitation.

Three experiments were made in which zinc cyanide and potassium sulphate were precipitated together in presence of so little water that only a small proportion of potassium sulphate would be dissolved by it. Five grams of zinc potassium cyanide were dissolved in 24 c.c. of water, and precipitated with a cold saturated solution containing 5·75 grams of zinc sulphate. The reaction is represented by the equation

$$ZnK_2(CN)_4 + ZnSO_4 = 2Zn(CN)_2 + K_2SO_4.$$

The precipitate was washed with cold water until no sulphate could be detected in the washings, and then dried. It now consisted entirely of zinc cyanide, and did not contain a trace of potassium sulphate. A similar experiment with potassium cyanide and zinc sulphate led to the same result. These experiments were now repeated, using zinc chloride instead of zinc sulphate, potassium chloride being formed instead of potassium sulphate, so that it might be ascertained whether this salt was entangled by the zinc cyanide precipitated with it. To diminish the solubility of potassium chloride in water, an alcoholic solution of zinc chloride was precipitated with a dilute alcoholic solution of potassium cyanide. The resulting precipitate was washed with dilute alcohol until the washings no longer contained chloride and then analysed. It consisted entirely of zinc cyanide, no potassium chloride having been retained.

These results conclusively show that zinc cyanide does not entangle salts which are precipitated with it. The retention of the mercuric cyanide by zinc cyanide must, therefore, be attributed to the existence of chemical attraction between the molecules of these salts, under the conditions which obtain during precipitation. The correctness of this conclusion has since been substantiated by a considerable mass of experimental evidence.

It has already been shown that cold water has no immediate action on the substance, but that after prolonged contact mercuric cyanide is very gradually dissolved. If the inability of the water to dissolve the mercuric cyanide is due to anything in the nature of a protective coating of zinc cyanide, a liquid in which zinc cyanide is insoluble but which dissolves mercuric cyanide much more readily than water, should also be unable to dissolve mercuric cyanide from the substance, whereas, if the mercuric salt were loosely combined with the zinc cyanide, it might be more readily dissolved by this liquid, especially if it contained a salt capable of forming a stable compound with the mercuric cyanide. A number of experiments were made with the object of finding some solution which would serve this purpose. Exactly the proper liquid was at last found in a strong aqueous solution of potassium iodide, in which mercuric cyanide is far more soluble than it is in water, owing to the formation of a soluble crystalline double salt of the formula $Hg(CN)_2,2KI$. The effect was therefore tried of digesting a material containing 36·5 per cent. of retained mercuric cyanide with a strong aqueous solution of potassium iodide. A weighed quantity (1·3 grams) was left in contact with 15 c.c. of the solution, at the ordinary temperature, for 24 hours. The precipitate was collected, washed with cold water until free from soluble mercuric salt and dried. On analysis, it was proved that the substance now consisted almost entirely of zinc cyanide, only 0·8 per cent. of mercuric cyanide being present. It is thus shown that whilst cold water, after digestion with the material for 24 hours, dissolves only about 1 per cent. of the mercuric cyanide, a strong solution of potassium iodide, acting under the same conditions, dissolves 35·7 per cent. of the salt, that is, practically the whole of the retained mercuric cyanide. From the filtrate, crystals were obtained whose composition corresponded with the formula $Hg(CN)_2,2KI$.

This result negatives the suggestion that the mercuric cyanide is encased by the zinc cyanide, and is in accordance with the conclusion that the material contains a compound of the two cyanides.

The Conditions which influence the Retention of Mercuric Cyanide.

An extended series of observations, as to the conditions which affect the retention of the mercuric cyanide in the precipitate, has not only confirmed this conclusion, but has furnished evidence which makes it possible to ascertain with considerable certainty what the composition of the double cyanide is.

Experiments have been made in which the various conditions attending precipitation have been modified in order to ascertain to what extent they determine the composition of the substance. It has been found that the order in which the two solutions are mixed does not appreciably affect the composition of the precipitate. Working with saturated aqueous solutions containing equimolecular proportions of mercuric potassium cyanide and zinc sulphate, the addition of the solution of zinc sulphate to that of the mercuric potassium cyanide furnished a precipitate which, after washing, contained 36·9 per cent. of mercuric cyanide, whilst when the mercuric potassium cyanide was added to the zinc sulphate the washed precipitate contained 37·7 per cent. of the mercuric salt.

A study of the influence of temperature has proved that the higher the temperature the smaller is the amount of mercuric cyanide retained by the precipitate. The experiments described above were repeated at 100°, boiling solutions of the reacting salts being mixed, so that the influence of temperature might be ascertained. The precipitate produced under these conditions contained 25·5 per cent. of mercuric cyanide, which is about 11 per cent. less than that resulting from interaction at about 15°. This difference probably corresponds with the increased solubility of the mercuric cyanide in the hot, as compared with the cold solution of potassium sulphate.

It now became of interest to determine the action of mass on the chemical change. For this purpose 1 mol. proportion of mercuric potassium cyanide was fractionally precipitated with 1 mol. proportion of zinc sulphate, the two solutions being prepared with as little water as possible, and the solution of zinc sulphate added in four equal parts. The precipitate was collected after the addition of each fourth part, and washed with cold water as before. The composition of the four precipitates was then ascertained by analysis. Two series of experiments were made in this way, the first at a rather lower temperature than the second, which accounts for the small differences in the two series of percentages. The details are given in the table, and the curves plotted from these results are shown in the diagram (Fig. 1).

Fractional Precipitation of Mercuric Potassium Cyanide (1 *mol.*) *with Zinc Sulphate* (1 *mol. added in* 4 *equal parts*). (Fig. 1, A and B.)

Series A. t = 10—13°.		Series B. t = 17—20°.	
¼ mol. $ZnSO_4$.	Per cent. $Hg(CN)_2$ in precipitate.	¼ mol. $ZnSO_4$.	Per cent. $Hg(CN)_2$ in precipitate.
1st	27·15	1st	25·7
2nd	31·95	2nd	31·2
3rd	34·37	3rd	34·0
4th	38·53	4th	38·0

The results show that there is a gradual increase in the percentage of retained mercuric cyanide in each fraction of the precipitate, the first fraction containing the least, and the last fraction the most, mercuric salt. When the reaction is carried out in this manner there are three variable conditions: (1) the amount of water, which increases with each addition of the solution of zinc sulphate; (2) the amount of potassium sulphate, which is also augmented by each addition of zinc sulphate; and (3) the amount of mercuric potassium cyanide, which diminishes relatively with each addition of zinc sulphate; the first fraction of the precipitate is formed by the interaction of $1ZnSO_4$ and $4HgK_2(CN)_4$, the second by the interaction of $1ZnSO_4$ and $3HgK_2(CN)_4$, the third by the interaction of $1ZnSO_4$ and $2HgK_2(CN)_4$, whilst the fourth fraction results from the interaction of $1ZnSO_4$ and $1HgK_2(CN)_4$. The largest percentage of mercuric cyanide is retained when reaction occurs in equimolecular proportions, but even then a large quantity of the mercuric cyanide, nearly three-fourths of the total quantity, appears in the precipitate in the free state and is subsequently washed away.

The variations in the composition of the precipitates cannot be principally attributed to the action of the water, since former experiments have shown that the larger the quantity of water present during the precipitation the smaller is the quantity of mercuric cyanide retained, whilst here, although the volume of water increases with each fractional precipitation, the amount of retained mercuric cyanide also increases, the smallest quantity being found when the volume of water is smallest, and the largest amount when the volume of water is greatest. It is clear that there must be some other influence at work in the opposite direction. It is improbable that the increase in the mass of the potassium sulphate will do more than slightly enhance the amount of mercuric cyanide, since it can only act by dissolving in the water and rendering it incapable of removing so much mercuric salt.

There remains for consideration the variation in the mass of the mercuric potassium cyanide. That this salt exerts an important influence on the course of the change is evident from the circumstance that the size of the first fraction is very much smaller than that of the precipitates subsequently formed. It is observable that the larger the proportion of this salt to that of one molecule of zinc sulphate the smaller is the percentage of mercuric cyanide retained. The maximum percentage is reached when the two salts are present in equimolecular proportions; that is to say, when there is sufficient zinc sulphate present to decompose the whole of the mercuric potassium cyanide, in accordance with the equation

$$ZnSO_4 + HgK_2(CN)_4 = Zn(CN)_2 + Hg(CN)_2 + K_2SO_4.$$

The action of excess of mercuric potassium cyanide on the precipitate appears to be represented by the equation

$$[xZnCN_2 + yHg(CN)_2] + HgK_2(CN)_4 = ZnK_2(CN)_4 + yHg(CN)_2 + xZn(CN)_2.$$

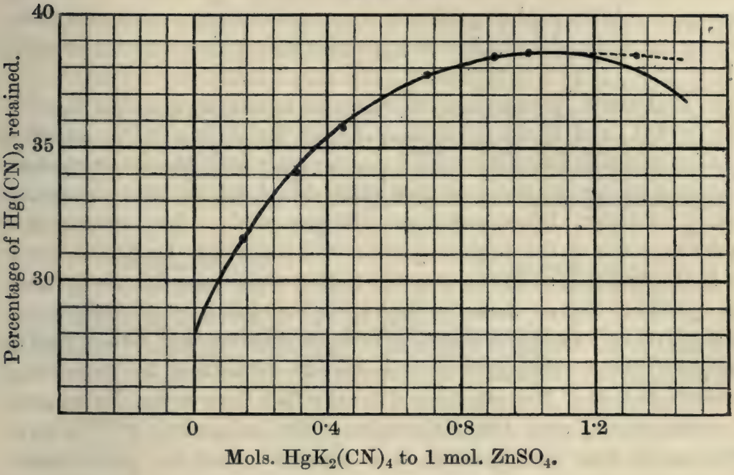
These results serve to exhibit the influence of excess of mercuric potassium cyanide on the composition of the precipitate. In another series the influence of excess of zinc sulphate was studied. In these experiments the action of one of the variables alluded to above was reduced to a minimum. The quantity of potassium sulphate was made as far as possible constant by saturating both the solution of mercuric potassium cyanide and that of zinc sulphate with this salt before mixing the two substances together, so that in every instance precipitation occurred in a liquid saturated with potassium sulphate. A cold saturated solution containing 45·5 grams (1 mol. proportion) of mercuric potassium cyanide was saturated with potassium sulphate. The volume of the solution was 75 c.c. Different volumes of the liquid were added to a saturated aqueous solution containing 9·8 grams (1 mol. proportion) of zinc sulphate; this solution being also saturated with potassium sulphate. The precipitates were collected, washed, dried, and analysed in the usual manner. The following are the results which were obtained; from them the curve in Fig. 2 has been plotted. Unlike the experiments in the former series, these do not represent a process of fractional precipitation; the solutions containing different amounts of the mercury salt being added each to a separate solution containing the 1 mol. proportion of zinc sulphate.

Precipitation of Solution of 1 *mol. proportion of* $ZnSO_4$ *with varying quantities of* $HgK_2(CN)_4$. (Fig. 2.)

Mols. of $HgK_2(CN)_4$ to 1 mol. $ZnSO_4$.	Percentage of $Hg(CN)_2$ retained in the precipitate.
0·146	31·58
0·30	34·02
0·446	35·82
0·7	37·74
0·9	38·40
1·0	38·50
1·31	38·44

In plotting these results the curve has been drawn, not by the free hand, but with a bent lath, in the manner suggested in his work on the properties of solutions by my friend Mr. Spencer Pickering, F.R.S., to whom I am indebted for much valuable information. It is interesting to observe that the first six experimental points lie perfectly on the curve made by the bent lath (the continuous line in Fig. 2), whereas the seventh point lies beyond this curve, thus indicating the existence of a change of curvature at or near the sixth point, which corresponds with the interaction of equimolecular proportions and the production of the maximum amount of retained mercuric cyanide. It is

FIG. 2.



clear that a change of curvature must occur here, for the conditions change at this point; the precipitation, which before was only partial, here becomes complete, and, of course, remains so at all points beyond. It may be inferred from the direction which the bent lath curve follows, that even if the conditions which obtained at the first six points before the equimolecular proportion was reached were continued, the maximum formation would still coincide with the point at which equimolecular interaction takes place, for the curve bends downwards after reaching the sixth point.

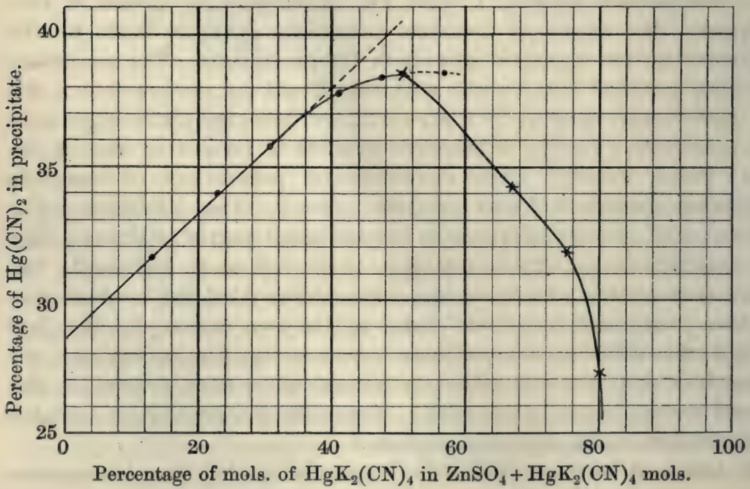
A comparison of Fig. 1 with Fig. 2 shows that excess of zinc sulphate, like excess of mercuric potassium cyanide, leads to the retention of less mercuric cyanide in the precipitate. The maximum quantity retained corresponds with that found in the previous series of experiments, namely, 38·5 per cent., and the precipitate containing the maximum quantity of mercuric cyanide is formed at exactly the same point, namely, when equimolecular proportions of mercuric potassium cyanide and zinc sulphate interact. The difference in the character of the two curves is to be attributed partly to the fact that the experiments to which they relate were not made in exactly the same manner, but chiefly to the circumstance that the environment of the precipitate is not the same in the two cases. In the first series, the salts in the solution surrounding the precipitate are potassium sulphate and mercuric potassium cyanide, whilst, in the second series, the solution which surrounds the precipitate contains potassium sulphate and zinc sulphate.

It has now been satisfactorily demonstrated that the phenomenon under investigation is the formation of double cyanide of zinc and mercury, insoluble in, but partially decomposed by, water. Can any evidence be obtained as to the composition and formula of this double salt?

The maximum percentage of retained mercuric cyanide is near 38·5 per cent., and by no device has it been found possible to appreciably augment this quantity, which corresponds with the interaction of equimolecular proportions of the salts dissolved in the minimum quantity of water. Since water must be present in order that reaction may occur, some of the double cyanide will inevitably be decomposed, even if the water is at first saturated with potassium sulphate or mercuric cyanide; for as soon as precipitation takes place the water which previously held the reacting salts in solution will be set free to decompose the double salt or prevent its formation by dissolving mercuric cyanide. Having regard to the fact that some decomposition must occur, and that, therefore, the substance will always contain some free zinc cyanide, it is probable that the pure double salt contains somewhat more mercuric cyanide than the maximum actually obtainable, viz., 38·5 per cent. The simplest molecular proportion, representing somewhat more than 38·5 per cent. of mercuric cyanide, is $Zn(CN)_2,\frac{1}{4}Hg(CN)_2$ or $Zn_4Hg(CN)_{10}$, which requires 40·65 per cent. of mercuric cyanide. Confirmatory evidence that this is really the formula of the double cyanide is

Fig. 3.

• = $HgK_2(CN)_4$ mols. added to $ZnSO_4$ mols.
× = $ZnSO_4$ mols. added to $HgK_2(CN)_4$ mols.



afforded by a closer examination of the curves representing the two series of results above described. For this purpose these two series of results have been plotted in one diagram (Fig. 3). In order to render this possible, the "percentage-molecular" plotting, suggested by Mr. Pickering, has been adopted in this diagram. The percentage numbers of molecules of mercuric potassium cyanide in the total number of reacting molecules are plotted against the percentages of mercuric cyanide retained in the precipitates. The numbers used are as follows:—

Left-hand curve.		Right-hand curve.	
Per cent. $HgK_2(CN)_4$ mols. in the $HgK_2(CN)_4 + ZnSO_4$ mols.	Per cent. of $Hg(CN)_2$ in precipitates.	Per cent. of $HgK_2(CN)_4$ mols. in the $HgK_2(CN)_4$ + $ZnSO_4$ mols.	Per cent. of $Hg(CN)_2$ in precipitates.
12·74	31·58	50·0	38·53
23·10	34·02	66·67	34·37
30·85	35·82	75·0	31·95
41·18	37·74	80·0	27·15
47·37	38·40	—	—
50·00	38·50	—	—
56·71	38·44	—	—

The following equations also illustrate the nature of the reaction depicted by the two branches and by the apex of the curves. In these equations the formula of the precipitate is assumed to be $Zn_4Hg(CN)_{10}$, although the facts which they indicate are independent of any particular formula.

I. $2(4ZnSO_4,xH_2O) + 1[4HgK_2(CN)_4,yH_2O]$ $= 1[Hg(CN)_2,4Zn(CN_2)] + 3[Hg(CN)_2] + [(2x + y)H_2O]$ $+ 1(K_2SO_4) + ZnSO_4$. Left-hand curve. Zinc sulphate in excess.

II. $1(4ZnSO_4,xH_2O) + 1[4HgK_2(CN)_4,yH_2O]$ $= 1[Hg(CN)_2,4Zn(CN)_2] + 3[Hg(CN)_2] + [(x + y)H_2O]$ $+ 4(K_2SO_4)$. Apex of curves. Equimolecular proportions interact.

III. $1(4ZnSO_4,xH_2O) + 2[4HgK_2(CN)_4,yH_2O]$ $= 1[Hg(CN)_2,4Zn(CN)_2] + 3[Hg(CN)_2] + [(x + 2y)H_2O]$ $+ 4(K_2SO_4) + 1[4HgK_2(CN)_4]$. Right-hand curve. Mercuric potassium cyanide in excess.

A glance at these equations shows that the amount of water per molecule of precipitate formed is least, and therefore the percentage of mercuric cyanide in the precipitate (which is partially decomposed by water) must be greatest, when the reagents are present in equimolecular proportions, the $(x + y)H_2O$ present in this case being always less than the $(nx + y)H_2O$ or $(x + ny)H_2O$ present in the other cases.

Moreover, reference to the diagram (Fig. 3) shows that, in accordance with this conclusion, the percentage of mercuric cyanide is actually greatest at the equimolecular proportion. As has already been pointed out, the two branches of the figure are not strictly comparable, owing chiefly to the presence of different substances in the two liquids in which the precipitate is formed; the results expressed by the right-hand branch are probably more complex than those of the left-hand branch, because of the presence in the former case of excess of mercuric zinc cyanide, which has a very marked action on the precipitate. The left-hand branch must, therefore, be taken as representing more simply the mass action of the water alone on the precipitate. Now the first three experimental points on this branch, where this action is further simplified by the smallness of the precipitate formed, lie on a nearly straight line; by prolonging this line (the dotted line in Fig. 3) to equimolecular proportions of the reagents, we arrive at the probable composition of the precipitate which would be formed in presence of the minimum quantity of water, if the reaction occurred under the same simple conditions which obtained in the first three experiments. The composition thus indicated is 40·5 per cent. of mercuric cyanide, a number which agrees almost exactly with the percentage (40·65) required by the formula $Zn_4Hg(CN)_{10}$. It may, therefore, be safely concluded that this is the formula of the double salt.

In the course of the numerous experiments which this inquiry has involved, no evidence has been obtained of the existence of any other compound of the two cyanides than that now described. A special experiment was made to ascertain whether the formation of the decacyanide is preceded by the production of a salt richer in mercury, such as that assumed by Gmelin, $ZnHg(CN)_4$. For it might be that this tetracyanide is formed according to the equation

$$HgK_2(CN)_4 + ZnSO_4 = HgZn(CN)_4 + K_2SO_4,$$

and subsequently breaks up into mercuric cyanide and the double decacyanide $4HgZn(CN)_4 = 3Hg(CN)_2 + Zn_4Hg(CN)_{10}$. A cold saturated solution of mercuric potassium cyanide was made to dissolve as much mercuric cyanide as possible, the liquid being digested for some hours with the mercuric salt finely powdered. A cold saturated solution of zinc sulphate was likewise made to absorb as much mercuric cyanide as it would take up. The solutions were then mixed, the precipitate collected and washed with a saturated aqueous solution of mercuric cyanide, and dried over calcium chloride and analysed. It contained 60 per cent. of mercuric cyanide; the formula $HgZn(CN)_4$ requires

68·29 per cent. When washed with cold water the precipitate behaved as if it contained free mercuric cyanide, mercuric salt being quickly dissolved in large quantity. The washing was continued until no more mercuric cyanide was removed, when the remaining precipitate was dried and analysed. It contained 38·8 per cent. of mercuric cyanide, which is only very slightly higher than the maximum percentage already determined, namely, 38·5. There is, therefore, no evidence that these two cyanides can combine in any but the proportion $4Zn(CN)_2 : Hg(CN)_2$. It is not to be expected that saturating the solutions with mercuric cyanide would prevent decomposition and cause any appreciable increase in the retention of mercuric cyanide, since directly precipitation commences the water in which the reacting salts were dissolved will be set free and will be able to attack the double salt and dissolve mercuric cyanide from it.

Attempts to Prepare the Double Salt in other ways.

It has already been shown that this double salt, $Zn(CN)_2,\frac{1}{4}Hg(CN)_2$, cannot be produced except by means of a process in which the two cyanides are precipitated together. It cannot be formed by heating at 100° the ready formed cyanides, either with or without water; neither does it result from the action of hydrogen cyanide on a mixture of mercuric oxide and zinc carbonate suspended in water or alcohol. These are the methods usually employed in forming soluble double salts.

It appears probable that the explanation of this remarkable fact may reside in the circumstance that combination cannot occur unless simple molecules, $Zn(CN)_2$ and $Hg(CN)_2$, are brought together. We know that these salts in the solid state are most probably composed of complex molecules of the formula $[Hg(CN)_2]_n$ and $[Zn(CN)_2]_n$. There seems to be no tendency on the part of these complexes to combine together. Similarly, the solid oxide of mercury and the solid zinc carbonate may be supposed to consist of complexes of the simple fundamental molecules HgO and $ZnCO_3$; and it appears that these are changed into masses of the solid cyanides by the action of hydrogen cyanide, and hence the double salt cannot be formed in this way. When, however, the two cyanides are precipitated from solution, we must suppose that at first the simple fundamental molecules are formed, and that combination takes place etween them in the proportion $4Zn(CN)_2 : Hg(CN)_2$ to an extent which is principally conditioned by the quantity of water present. Many of the fundamental molecules unite with each other to form the molecular aggregates which constitute the solid zinc cyanide; whilst those of the mercuric cyanide not required for the production of the double salt also aggregate as solid particles, although some which would otherwise enter into combination with zinc cyanide dissolve in the water. When the precipitate is washed with cold water, the uncombined and undissolved solid particles of mercuric cyanide are removed, but the double salt, which is always mixed with zinc cyanide, is scarcely attacked by the cold water.

Several attempts have been made to experimentally verify the hypothesis that the formation of the double cyanide is the result of combination between fundamental molecules. The undoubted fact that dilute solutions contain these simple molecules suggested the possibility of preparing the compound by mixing dilute solutions of the two cyanides. Unfortunately this method cannot be actually carried out, for although a dilute solution of mercuric cyanide in several solvents can be made, it has not been found possible to dissolve zinc cyanide without at the same time decomposing it. This salt is insoluble in water, alcohol, and the usual solvents, and no liquid could be found in which it would dissolve without combination or decomposition. Spontaneous evaporation of a solution of mercuric cyanide with freshly precipitated zinc cyanide led to no result.

It is highly probable that a dilute solution of metallic zinc in mercury contains monatomic zinc molecules, and if the solution is heated it is likely that some monatomic molecules of mercury will also be formed. If, now, cyanogen gas were led into this hot solution and combination occurred, there would be present, at first at all events, fundamental molecules of the two cyanides of zinc and mercury which, it is to be expected, would combine to form the double salt. Many experiments have been made in this manner with dilute solutions of zinc in mercury at all temperatures up to and including the boiling point, but they all failed to afford any of the double salt. The white solid which separated from the mercury was found to be almost entirely zinc cyanide. The cyanogen had not combined with the mercury to any appreciable extent.

As both mercuric cyanide and zinc cyanide are resolved into the metal and cyanogen when strongly heated, it appeared possible that if a mixture of the two salts were heated in a closed and vacuous tube, so that a certain quantity of each cyanide is decomposed, that during the recombination which would take place on cooling some of the double cyanide might be produced. Numerous experiments of this kind failed, however, to afford any of the substance, owing, apparently, to the polymerisation of the cyanogen, which invariably occurred when the temperature was elevated enough to decompose zinc cyanide.

So far, then, it has not been found possible to prepare the double salt in any other way than by precipitation.

Search for Similar Double Cyanides of other Metals.

A large number of experiments have been made in order to ascertain whether any other insoluble double cyanide analogous to this mercuric zinc cyanide can be prepared by the union of mercuric cyanide with other metallic cyanides. These experiments were, as a rule, carried out in the following manner. A cold saturated solution of mercuric potassium cyanide was decomposed with a cold saturated solution containing an equimolecular proportion of the metallic salt, and any precipitate that formed was analysed after it had been washed with cold water.

Cadmium.

On the addition of a saturated solution of cadmium chloride to a saturated solution of mercuric potassium cyanide, a white precipitate is thrown down. When washed with cold water, this precipitate dissolves, and, on evaporating the solution at 100°, decomposition sets in with evolution of hydrogen cyanide. If, however, the precipitate is dissolved in water at 20° and the solution cooled below 0°, crystals separate. These were purified by recrystallisation, and dried over calcium chloride. They contained 56·9 per cent. of mercury; the formula $Cd(CN)_2,1\frac{1}{2}Hg(CN)_2$ requires 55·35 per cent. The double cyanide of cadmium and mercury is, therefore, a soluble salt which differs from zinc mercuric cyanide both in composition and properties.

Nickel.

A cold saturated solution of mercuric potassium cyanide was decomposed with a saturated solution containing an equivalent quantity of nickel chloride. A bulky, green precipitate was thrown down which was washed with cold water. It was afterwards examined, but it contained no mercuric salt, all of which was found in the filtrate and washings.

Aluminium.

By the addition of a saturated solution of soda-alum to a saturated solution of an equivalent quantity of mercuric potassium cyanide, an abundant, gelatinous precipitate was thrown down, whilst much hydrogen cyanide was evolved. The washed precipitate contained no mercury.

Magnesium.

When saturated solutions containing equivalent quantities of magnesium sulphate and mercuric potassium cyanide are mixed, no precipitate is formed. On warming the solution, decomposition begins with evolution of hydrogen cyanide.

Silver.

A saturated solution of mercuric potassium cyanide was decomposed by adding a saturated solution containing an equivalent proportion of silver nitrite. An abundant, white precipitate resulted, and this, after washing with cold water, consisted of pure silver cyanide.

Lead.

On decomposing a saturated solution of mercuric potassium cyanide with a saturated solution of lead acetate, a small, white precipitate was obtained, which, after washing, contained no mercury.

Manganese.

Saturated solutions containing equivalent quantities of mercuric potassium cyanide and manganous chloride were mixed together in the cold. Much hydrogen cyanide was evolved, and only a small precipitate was obtained, which, after it had been washed, contained no mercury.

Copper.

A solution of copper sulphate energetically reacts with a solution of mercuric potassium cyanide; some gas is evolved, and the mixture becomes semi-solid. After washing the mass with cold water until it was free from soluble mercuric salt, no mercuric salt remained.

Tin.

The solution of mercuric potassium cyanide was decomposed with the equivalent quantity of stannic chloride, dissolved in the smallest possible quantity of water. A great deal of hydrogen cyanide was given off, and the precipitate which formed was almost entirely dissolved by washing with cold water, whilst the residue contained no mercury. On cooling the filtrate below 0°, flat, tabular crystals were deposited, which were dried in a vacuum over calcium chloride. These crystals fused when heated, a little water being evolved. By qualitative analyses they were found to contain mercury, potassium, cyanogen, and chlorine, but no tin. The percentage of mercury present in them was ascertained to be 59·75; the formula

$$Hg(CN)_2,KCl,\tfrac{1}{2}OH_2$$

requires 59·5 per cent.

From the negative results of these experiments with various metallic salts, it appears that the *tetrazincic monomercuric decacyanide*,

$Zn_4Hg(CN)_{10}$, is an exceptional compound, no similar compound of mercuric cyanide with other metallic cyanides having been obtained when experiments were made under conditions exactly corresponding with those which led to the formation of the mercuric zinc cyanide, which this inquiry has shown must be included in the little known class of insoluble double salts.

LX.—*Note on Diastatic Action.*

By E. R. Moritz, Chemist to the Country Brewers' Society, and T. A. Glendinning.

In the course of some technical investigations by one of us (*Brewing Trade Review*, 1891, 6), it was found that brewers' worts, as they issue from the mash-tun, remain constant in respect to their starch-transformation products when digested for two hours at the same temperature as that at which the conversion was conducted. The diastase in these solutions therefore exercises (within the above period) no action upon the starch products contained in it. But if fresh starch be added to these solutions, the diastase (which we may term "residual" diastase) is found to possess considerable energy in liquefying and saccharifying it, although it appeared from these experiments that the energy of this residual diastase is distinctly inferior to that of the original malt. The comparison between the energy of the original and of the residual diastase was estimated, in the investigation referred to, by rough volumetric methods, and it appeared to us of interest to determine more accurately the extent to which the added starch is acted upon by the residual diastase. The following experiments were made to elucidate the question:—The preparation of the malt extract (diastase solution) and of the starch paste, as well as the analyses of the transformation products, were carried out exactly as laid down in the researches of Brown and Heron (Trans., 1879, 596). The plan of the first experiment was as follows:—

A conversion was made by digesting 5 grams of starch made into paste with 5 c.c. of normal malt extract at a given temperature for two hours. The volume of the solution during conversion was 175 to 180 c.c. At the expiration of the converting period, the conversion was quickly cooled and made up to 200 c.c. at 15·5°; a portion was abstracted for analysis, further diastatic action being arrested in it by the addition of salicylic acid. Half the volume of the conversion was used as the converting agent for a fresh lot of starch paste (2·5 grams).

This second conversion was conducted at the same temperature as the first, and for the same time. A portion of this second conversion was abstracted and analysed as before, and one-half the volume now used as the converting agent for a third lot of starch paste (1·25 grams), which was again digested at the previous temperature, and for the same time, and then analysed. In the second and third transformations, the amount of starch paste and malt extract clearly bear the same relation to each other as in the first.

The transformation products are all expressed as $K_{3\cdot86}$, that is, in terms of the cupric reducing power of the solid matter in solution referred to pure dextrose taken as 100; the volumes taken for analysis are referred to weights from determinations of their sp. gr. at 15·5°. The first conversion will, besides maltose, contain reducing sugars, due to the malt extract; the total reducing power of the conversion is therefore corrected for this by determining the reducing matters in the malt extract used, after digesting it for the same time, and under the same conditions as the first conversion. The second and third conversions will contain (besides some of the reducing sugars from the malt extract) an abundance of maltose, formed, in the case of the second conversion, from the first, in the case of the third conversion, from the second. The second and third conversions are, therefore, corrected by determining and deducting the reducing matters in portions of the first and second transformations, after digestion for the same time, and under the same conditions, as the second and third transformations respectively. In the second conversion, the total reducing power is therefore corrected by that of the first conversion added, *plus* that due to any increase in it incident to a further digestion for two hours. Similarly with the third conversion. The solid matter of the first conversion is corrected by that of the malt extract used; that of the second by the solids of the first, and so on. The following figures give our results, after making the various corrections above described:—

Series I.—Digestions for two hours; ratio of malt extract to starch, 1 c.c. to 1 gram; this ratio maintained constant. Temperature of transformations, 52°* throughout.

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* The above temperature was selected for this series as being the optimum one for diastatic energy. In some of the later conversions, the malt extract was momentarily heated at the transformation temperature before use. This was not done throughout Series I, as at the temperature employed there is no weakening of the diastase by subjection to that temperature beforehand. Thus, even when heated at 52° for three hours previous to employment, malt extract converted starch at 52° (ratio 1 c.c. to 1 gram) to a K of 48·6, and to a K of 48·0 when the ratio was 1 c.c. to 3 grams. These figures agree so closely with those of Series I, in which malt extract was unheated previous to transformation, that the influence of

		$K_{3\cdot 86}$.
A.	First conversion	48·7
	Second conversion (transformed with first)	48·6
	Third conversion (transformed with second)	48·4
B.	First conversion	48·5
	Second conversion (transformed with first)	48·6
	Third conversion (transformed with second)	48·4
C.	First conversion	48·5
	Second conversion (transformed with first)	48·0
	Third conversion (transformed with second)	48·2

Under the conditions of the above experiments, the "residual" diastase is not only very vigorous, but its vigour is exactly equal to that of the original diastase. Later experiments show that this is not invariably the case; in this instance, the equality in vigour between original and residual diastases is due to the relatively high ratio of malt extract to starch, and to the employment of an optimum temperature. Of these favouring causes, the former is found to be the less important. This is in some measure indicated by three independent transformations, carried out, as before, at 52°, but where the whole of the starch paste previously used (15 grams) is converted at once (instead of being previously added) by 5 c.c. of malt extract. The ratio of malt extract to starch is now 1 : 3. The digestions are two hours, as before, and the corrections for malt extract, &c., applied as previously described. The following are the results:—

	$K_{3\cdot 86}$.
D	48·4
D_1	48·5
D_2	48·1

The products of these conversions are identical with those of A, B, and C, in spite of the lowering of the malt extract by two-thirds of the previous amounts.

Such influence as is exercised by the ratio of malt extract is more plainly seen in Series II. The transformations were carried out again at the optimum temperature (52°), and under the same conditions as in Series I, excepting that in the second and third transformations of each set, the starch is transformed by progressively diminishing portions of first conversion.

Series II.—Transformations at 52° for two hours.

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such preparatory treatment, when subsequently converting at optimum temperatures, may be neglected.

	Ratio of malt extract to starch.	$K_{3\cdot 86}$.
A. First conversion	1 c.c. : 1 gram.	48·4
Second conversion (transformed with first)	1 c.c. : 2 grams.	48·5
Third conversion (transformed with first)	1 c.c. : 4 grams.	47·7
Fourth conversion (transformed with first)	1 c.c. : 10 grams.	40·1
B. First conversion	1 c.c. : 1 gram.	48·7
Second conversion (transformed with first)	1 c.c. : 2 grams.	48·7
Third conversion (transformed with first)	1 c.c. : 4 grams.	46·6
C. First conversion	1 c.c. : 1 gram.	48·3
Second conversion (transformed with first)	1 c.c. : 4 grams.	46·8
Third conversion (transformed with first)	1 c.c. : 10 grams.	41·8

From these experiments, it is clear that diminishing the relative amount of malt extract to starch does to some extent reduce the vigour of the residual as compared with that of the original diastase, but not very markedly, and certainly not to an extent proportional to the diminution. The influence of temperature upon the energy of residual diastase is far more marked, and is shown in Series III and IV. In these series, the same conditions are adopted as in Series I, the ratio of malt extract to starch being high, and maintained constant throughout; but the temperatures of transformation adopted throughout being such as to restrict the full vigour of the diastase.

Series III.—Ratio of malt extract to starch 1 c.c. to 1 gram; maintained constant throughout. Transformations conducted throughout at 61°, malt extract previously heated to 63°.* Other details exactly as in Series I.

	$K_{3\cdot 86}$.
A. First conversion	45·3
Second conversion (transformed with first)	36·9
Third conversion (transformed with second)	24·3
B. First conversion	46·4
Second conversion (transformed with first)	37·8
Third conversion (transformed with second)	28·2

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* The difference of 2° between the temperature of transformation and that to which the malt extract is previously heated, permits of a slight accidental rise during

Series IV.—As above, but conversions at 66°; malt extract previously heated to 68°.*

	$K_{3\cdot 86}$.
First conversion	38·4
Second conversion (transformed with first)	28·8
Third conversion (transformed with second)	22·5

In these series there is a very marked discrepancy between the vigour of the "residual" and of the original diastase. Previous experiments indicated that this is rather attributable to the restrictions of the diastase by the higher temperatures than to any deficiency in the quantity of malt extract used. But to place the cause of this diminution of vigour of residual diastase beyond doubt, the following experiments were made. A restricted conversion was conducted at 61° with malt extract previously heated to 63°; the second conversion was, however, conducted with a *larger* amount of malt extract than the first. The following results were obtained:—

	Ratio of malt extract to starch.	$K_{3\cdot 86}$.
First conversion	1 c.c. : 1 gram.	46·4
Second conversion (transformed with first)	2 c.c. : 1 gram.	35·6

The decrease in the vigour of the residual as compared with original diastase is therefore as marked as in Series III, where the temperatures adopted were the same as here, but where the amount of malt extract was not increased. It is a reasonable presumption, therefore, that the cause of the decrease in diastatic vigour must be sought in the temperature. That this is so is clearly shown by the following experiment; the starch paste was transformed at 61° by malt extract previously heated to 63°, *and kept at that temperature for three hours.* Ratio of malt extract to starch, 1 c.c. to 1 gram; period of digestion, two hours. The $K_{3\cdot 86}$ of this transformation was 38·5. The $K_{3\cdot 86}$ of two similar transformations at similar temperatures, but where malt extract was only momentarily taken to 63° and then quickly cooled, was 45·3 and 46·4 respectively. The marked decrease in the vigour of the diastase in those experiments where a decrease is found is therefore essentially to be attributed to the influence of a *protracted* subjection to a temperature in excess of the optimum; such influence being more pronounced where malt extract *alone* is exposed to temperatures exceeding the optimum than where (as during

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transformation without interference with results. The malt extract is momentarily heated to the required temperature, and is then quickly cooled to 15·5°.

* See previous note.

transformations) it is exposed to them when mixed together with starch or starch products.

Incidentally it may be added that in conducting transformations with different kinds of starch, the source of the starch was found to be an important factor in determining the extent to which it becomes hydrolysed by a given volume of malt extract in a given time under given conditions. With the three kinds of starch experimented upon, we found that the starch which gelatinises at the lowest temperature is hydrolysed to the greatest extent. The following results bear this out.

Temperature, 52°; 5 grams starch transformed with 10 c.c. of normal malt extract.

	$K_{3\cdot86}$		Gelatinising temperatures (approximate).
	Series I.	Series II.	
Potato starch	49·6	49·6	65°
Maize ,, ...	45·9	46·4	75°
Rice ,, ...	43·2	43·3	80°

Note.—Some of the above results are of some importance in regard to the operations of brewing. During the "mashing" or conversion of malted grain, a certain amount of starch is only rendered available for conversion some time after the attainment of the resting stage in the transformation of the main bulk of starch which is converted during the early stages of the process. Were the transformations carried out at the optimum temperatures in respect to diastatic vigour, there is reason to believe, from the results of Series I, that the "later" starch (if it may be so termed) would be converted by the "residual" diastase to the point reached by the early transformation. But practical operations being always conducted at temperatures restrictive of the full activity of the diastase, it is clear, from the results of Series III and IV, that the residual diastase is incompetent to hydrolyse the "later" starch to the same point to which the original starch is transformed. Occasionally the difference in the conversion products in the early and late stages of conversion gives rise to practical difficulties, and it is sought to overcome them by reserving some of the early worts for intermixture and digestion with the later worts, with the object of transforming the latter to the same point as the former, by means of its residual diastase.

The results of Series III and IV indicate that this action would be only an incomplete one, the residual diastase of the early wort having been weakened by subjection for some time to a temperature adverse to its continued vigour. That this is actually so is shown by the following experiments. The weak later worts were digested with strong first worts for two hours; the digestions were carried out at a lower temperature than that at which either wort was prepared. The reducing power of both strong and weak worts was determined after digesting for the same time and at the same temperature as the mixture; the results given in the last column are corrected for the reducing power of the strong wort added:—

	Ratio of strong to weak wort.	Approximate temperature of strong wort on leaving mash-tun.	Approximate temperature of weak wort on leaving mash-tun.	$K_{3\cdot86}$		
				Strong.	Weak.	After mixture and digestion.
a	1 : 5	67·7	67·2	40·6	36·7	39·6
b	1 : 10	67·2	66·6	38·2	29·9	33·2
c	1 : 10	67·2	66·6	39·1	30·6	35·6
d	1 : 10	68·3	68·8	43·3	30·7	34·8

The solid matters in the weak worts ranged from 1·5 to 3 grams per 100 c.c.; those in the strong from 21 to 24 grams per 100 c.c.; the ratio of 1 vol. strong to 10 vols. weak wort is therefore a high one. In spite of the relatively large amount of strong wort (and therefore of "residual" diastase), the starch products of the weak wort are not in any case carried to the same point as that to which the original starch was converted. These experiments have a special bearing upon the operations of brewers and distillers who employ unmalted as well as malted grain, but these considerations are of too technical a nature to be entered into here.

We consider that our results entitle us to form the following conclusions:—

The attainment of a resting stage in the transformation of starch by diastase by no means shows that the energy of the diastase is exhausted. The energy of this "residual" diastase is, in fact, very considerable, even under conditions adverse to its activity. It is somewhat weakened by increasing the amount of starch it has to convert, but it is weakened to a marked extent by subjecting it for some time to a temperature exceeding the optimum one for saccharification, especially when it is subjected alone, and unmixed with starch or starch products. When, however, it is not exposed for any length of time, whether previous to the first or to subsequent transformations, to a temperature exceeding the optimum, it appears capable, after transforming a considerable amount of starch, to transform further quantities to nearly the same point, when such further quantities are added successively and subsequent to the attainment of the resting stage in the preceding transformation.

LXI.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF EDINBURGH.

No. VII. *The Dissociation Constants of Organic Acids.*

By JAMES WALKER, D.Sc., Ph.D., F.R.S.E.

THE physical properties of chemical compounds have been classified in three groups—additive, colligative, and constitutive. The only purely additive property is mass: each element in a compound contributes its own mass to the total, so that the mass of the compound is the sum of the masses of its constituents. Other properties which are essentially additive are the specific heat, specific volume, and specific refractive power; but in all these cases a disturbing influence is apparent—similar atoms do not always contribute the same amount to the total, but the quantities vary according to the function exercised by the atoms in the compound. Thus, carbonyl oxygen has a value for the atomic volume different from the value attributed to hydroxyl oxygen; and so it is with other elements. Here the additive character of the property is modified by *constitution.* This influence is still more marked in properties such as the boiling point, melting point, colour, and crystalline form, so that these properties have been termed *constitutive.* The third group of properties consists of those which are independent of the nature, number, and arrangement of the atoms in the compound, and which assume the same value for the molecules of all compounds, no matter how these may be constituted. Examples of such *colligative* properties are the volume occupied by gases under fixed conditions of temperature and of pressure, and the depression of the freezing point of solutions.

Substances that are prepared in the course of a chemical investigation can only be identified by means of their own physical properties or by those of other substances into which they may be transformed. The first step is to ascertain the composition of the compound by some method of analysis; here advantage is taken of the additive character of mass. Next, the molecular weight is determined from some colligative property, for example, from the vapour density, the depression of the freezing point or elevation of the boiling point of some liquid in which the substance is dissolved. The only problem which remains is the determination of the arrangement of the atoms within the molecule—that is, the constitution. As a rule, chemical methods are resorted to for the strict solution of this problem, the substance being transformed into some other of known constitution. It is possible, however, to make use of constitutive properties for the same purpose, and the boiling point, the melting point, the colour, or the crystalline form of the compound may afford valuable, and even conclusive, information.

A property which is eminently dependent on the constitution, easy of accurate measurement, and generally applicable to the large class of organic acids, has of late years been brought forward by the theoretical and experimental work of Ostwald. This is the electrical conductivity of acids in dilute aqueous solution.

Arrhenius, in 1884, pointed out the existence of a remarkable parallelism between the electrolytic conductivity of acids, and their affinity as measured by any of the ordinary methods of chemical dynamics. The proportionality of the two properties is fully accounted for by the theory of electrolytic dissociation. According to this theory (which was first advanced to explain the phenomena of electrolytic conductivity in solutions), salts, acids, and bases, when dissolved in water, are more or less split up into electrically charged molecules or ions. Hydrogen, metals, and metallic radicles such as ammonium, NH_4, are charged, according to Faraday's law, with positive electricity, whilst hydroxyl and acid radicles are similarly charged with negative electricity. Hydrogen chloride, for example, is supposed to exist in dilute solution almost entirely as charged ions, $\overset{+}{H}$ and $\overset{-}{Cl}$; the charged hydrogen atoms being independent of the charged chlorine atoms, except in so far as the electrical charges prevent the concentration by mechanical means of any one kind of atom in a particular portion of the solution. Now, acids in aqueous solution are supposed to act as acids solely in virtue of the hydrogen ions they produce, and the more hydrogen ions a given quantity of acid (reckoned in equivalents) will produce, the stronger is that acid. But the hydrogen ions, besides their chemical activity, have also the power of carrying electricity, and the more there are present in a solution, the more electricity will be conveyed, that is, the greater will be the conductivity of the solution. In this way, it may be seen how the affinity, or strength, of an acid goes hand in hand with its electrical conductivity.

Whilst the molecular conductivity* of strong acids varies little with the concentration of the solution, that of weak acids increases considerably as the concentration diminishes, varying approximately as the square root of the dilution, or the number of litres in which one gram-molecular weight of the acid is contained. Ostwald, however, by the consistent use of the theory of electrolytic dissociation and the ordinary chemical law of mass action, arrived at an expression involving the conductivity, which is independent of the dilution at which the measurement is made.

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* The molecular conductivity of a substance in a given solution is equal to cv/r, where r is the resistance of the solution, v the number of litres in which 1 gram-molecule of the acid is contained, and c the constant of the electrolytic apparatus.

From his investigations of the conductivity of salts and strong acids at extreme dilutions, Kohlrausch found that the molecular conductivities of these substances reach a maximum value at a certain dilution, and thereafter remain constant, although the dilution is increased. The maximum value of the molecular conductivity for each substance is composed of two terms: one depending on the positive ion, the other on the negative ion. This behaviour is accounted for on the dissociation theory in the following manner:—The conductivity of a solution depends only on the number and the speed of the ions which it contains. At a given temperature the speed, in dilute solutions, is constant, so that if the molecular conductivity increases with the dilution, the increase can only be on account of an increase in the number of the ions, that is, on account of the increased dissociation of the dissolved substance. When the molecular conductivity no longer increases as the dilution proceeds, but remains stationary, this is due to the dissolved substance being entirely split up into its ions, and now the maximum molecular conductivity is determined solely by the speed of the ions. The numbers found by Kohlrausch to be characteristic of each ion thus represent the velocities of the ions, and the molecular conductivity of any substance, when it is entirely dissociated, may be numerically stated as the sum of the velocity-numbers pertaining to its ions. It is only in the case of salts and of powerful acids and bases, such as hydrogen chloride and potassium hydroxide, that values for the maximum molecular conductivity can be determined: weak acids and weak bases give values which still increase at the utmost attainable dilutions. Although, therefore, the maximum molecular conductivities of weak acids cannot be directly determined, it is yet easy to assign values to them by making use of the considerations mentioned above.

The maximum molecular conductivity of the sodium salt of the weak acid may be determined directly: from this there is subtracted the number which represents the speed of the sodium ion—the remainder represents the speed of the negative ion or acid radicle. This remainder added to the number which gives the speed of the hydrogen ion—found from observations with strong acids such as hydrogen chloride—furnishes the molecular conductivity at infinite dilution, that is, the maximum conductivity. Ostwald (*Zeit. physikal. Chem.*, **2**, 840), from the examination of a great number of sodium salts of various acids, has been able to state certain rules connecting the composition of acid radicles and their velocities, so that it is in general unnecessary to observe directly the molecular conductivity of the sodium salt of an acid to be investigated, the speed of the negative ion being ascertainable with sufficient accuracy from its composition.

The molecular conductivity of an acid at infinite dilution being thus determined, its molecular conductivity at any other dilution can only differ from this in virtue of there being relatively fewer ions in the solution to carry the electricity, for the speed of the ions does not vary, and each ion always carries the same charge. It is thus evident that the molecular conductivity is proportional to the amount of electrolytic dissociation, and the ratio of the molecular conductivity at the dilution v to the molecular conductivity at infinite dilution, that is, the ratio $\frac{\mu_v}{\mu_\infty} = m$, gives at once the degree of dissociation, or proportion of the whole dissolved substance which is dissociated.

Now, according to the general law of mass action, the product of the active masses of the dissociated ions must be proportional to the active mass of the undissociated acid. Suppose the volume in which one gram-molecule of a monobasic acid is contained to be v, then the mass of the acid in this volume is represented by 1. Of this, the proportion dissociated is m, and the proportion undissociated, $1 - m$. The active mass of each product of dissociation is m/v, and of the undissociated acid, $\frac{1-m}{v}$. Therefore, according to the principle of mass action above referred to—

$$\frac{m}{v}\frac{m}{v} = k\frac{1-m}{v},$$

where k is a constant, or

$$\frac{m^2}{(1-m)v} = k.$$

The constant k is the dissociation or affinity constant of Ostwald, and is, for any one acid, independent of the dilution. It represents, numerically, the reciprocal of twice the dilution at which the acid is half dissociated. As its value in the units adopted is inconveniently small, a constant K, 100 times greater, is usually chosen as the affinity constant.

Ostwald (*Zeit. physikal. Chem.*, **3**, 170, 241, 369) determined this constant for over 240 acids, and since his fundamental research other investigators have been at work on the same subject. The principal papers which have appeared are those of Bethmann (*Zeit. physikal. Chem.*, **5**, 385); Bader (*ibid.*, **6**, 289); and Walden (*ibid.*, **8**, 433). At present more than 400 acids have been studied with respect to this affinity constant, and many interesting relations between the values of the constant and the composition and constitution of the acids have been discovered. In the following pages are collected the results of a few more observations, which partly confirm these relations, and partly bring new regularities to light.

The method of measurement adopted was precisely that described by Ostwald (*Zeit. physikal. Chem.*, **2**, 561), the resistance being determined by means of a Wheatstone bridge and telephone. The temperature of experiment was kept constant throughout at 25°. No special precautions were taken in preparing the water used for making and diluting the solutions; it was the distilled water employed for general laboratory use.

The quality of the Edinburgh water for electrolytic purposes is excellent, one distillation being sufficient to give a liquid the conductivity of which compares favourably with that of most waters specially prepared for the purpose. The correction for the conductivity of the water was applied according to the method suggested by Arrhenius (compare Ostwald, *Zeit. physikal. Chem.*, **2**, 567), and amounted, on the average, to two units on the molecular conductivity at a dilution of 1000 litres.

In the following tables the letters employed have the significations noted below:—

v = dilution; that is, the number of litres of solution which contain one molecular weight of the acid in grams,
μ_v = the molecular conductivity in Siemens' units at the dilution v,
μ_∞ = the molecular conductivity at infinite dilution;
m = the degree of dissociation, μ_v/μ_∞;
k = the dissociation constant, $\dfrac{m^2}{(1-m)v}$;
K = the most probable value of $100k$.

Pimelic Acid, $HOOC\cdot[CH_2]_5\cdot COOH$.

$\mu_\infty = 351$.

v.	μ.	$100m$.	$100k$.
47·3	13·8	3·94	0·00342
94·6	19·4	5·50	0·00340
189·0	27·1	7·72	0·00342
378·0	37·6	10·71	0·00340
756·0	52·7	15·02	0·00351

K = 0·00342.

Walden found the value K = 0·00345 for a preparation from the same source.

Alkyl Derivatives of Pimelic Acid.

I am indebted to Professor W. H. Perkin, jun., for the following preparations of pimelic acid and its *ωω′*-alkyl derivatives. They were obtained from the ethereal salts of pentanetetracarboxylic acid and its corresponding substitution products.

Although pimelic acid is bibasic, it behaves, like all other weak bibasic acids, precisely as a monobasic acid, so far as dissociation in aqueous solution is concerned. The ions formed are, in the first place, $\overset{+}{H}$ and $OOC\cdot[C\overset{-}{H}_2]_5\cdot COOH$, not $\overset{+}{H}$, $\overset{+}{H}$, and $OOC\cdot[\overset{-}{C}\overset{-}{H}_2]_5\cdot COO$. The hydrogen atom of the second carboxyl group of a bibasic acid does not, as a rule, begin to be dissociated until about half of the hydrogen of the first carboxyl group has been split off. It may be seen from the table, that even at a dilution of 756 litres, only 15 per cent. of the first carboxyl hydrogen has been split off, so that we are still far from the limit at which the second carboxyl group is attacked.

ωω′-Dimethylpimelic Acid, $HOOC\cdot CH(CH_3)\cdot[CH_2]_3\cdot CH(CH_3)\cdot COOH$.

$\mu_\infty = 350.$

v.	*μ.*	100*m.*	100*k.*
128·0	22·1	6·31	0·00332
256·0	31·3	8·94	0·00343
512·0	43·4	12·40	0·00339
1024·0	59·4	16·97	0·00339

K = 0·00339.

ωω′-Diethylpimelic Acid, $HOOC\cdot CHEt\cdot[CH_2]_3\cdot CHEt\cdot COOH$.

$\mu_\infty = 350.$

v.	*μ.*	100*m.*	100*k.*
155·0	24·6	7·03	0·00343
310·0	34·5	9·86	0·00348
620·0	47·7	13·63	0·00347
1240·0	64·8	18·52	0·00340

K = 0·00345.

ωω′-Dipropylpimelic Acid, $HOOC\cdot CHPr\cdot[CH_2]_3\cdot CHPr\cdot COOH$.

$\mu_\infty = 350.$

v.	*μ.*	100*m.*	100*k.*
1114·0	60·5	17·3	0·0033
2228·0	81·9	23·4	0·0032
4456·0	109·2	31·2	0·0032

K = 0·0032.

Owing to the very sparing solubility of this acid in water at 25°, the dilutions at which the measurements were obtained are very great, which somewhat impairs the accuracy of the results; the conductivity of the water employed bearing a large proportion to the total conductivity, and the apparatus being less sensitive with great resistances. Another determination confirmed the numbers given above, the result being K = 0·0031.

ωω'-Diisopropylpimelic Acid, $HOOC{\cdot}CHPr^{\alpha}{\cdot}[CH_2]_3{\cdot}CHPr^{\alpha}{\cdot}COOH$.

$\mu_\infty = 350.$

v.	*μ*.	100*m*.	100*k*.
237·0	29·2	8·34	0·00320
474·0	40·2	11·5	0·00315
948·0	56·0	16·0	0·00321
1896·0	77·3	22·10	0·00330

K = 0·0032.

ωω'-Dibenzylpimelic Acid, $HOOC{\cdot}CH(C_7H_7){\cdot}[CH_2]_3{\cdot}CH(C_7H_7){\cdot}COOH$.

$\mu_\infty = 350.$

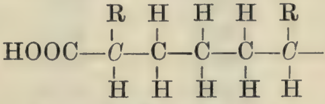
v.	*μ*.	100*m*.	100*k*.
2200·0	96·9	27·7	0·0048
4400·0	126·5	36·2	0·0047

K = 0·0048.

The value for the dibenzyl derivative is again somewhat doubtful, on account of the extremely slight solubility of the acid.

The following table contains the results obtained for the foregoing acids :—

Acid.	K.
Pimelic	0·00342
Dimethylpimelic	0·00339
Diethylpimelic	0·00345
Dipropylpimelic	0·0032
Diisopropylpimelic...........	0·0032
Dibenzylpimelic	0·0048

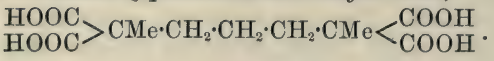
As a rule, the introduction of alkyl groups into a bibasic acid, increases the constant of the acid, and this is notably the case with succinic acid; but when the carboxyl groups are separated by a number of carbon atoms the effect of the introduction of an alkyl group is much diminished. Thus, Walden (*loc. cit.*, p. 488) found values for the alkyl-substituted glutaric acids which varied from 0·0052 to 0·0059, the value for glutaric acid itself being 0·00475 (Ostwald). Much the same behaviour characterises the substituted pimelic acids; the values of the dissociation constants approximate closely to that of the parent acid, with the doubtful exception of dibenzylpimelic acid. The radicle benzyl, however, is, in general, much more acid in its nature than the radicles of the saturated alcohols of the fatty series, that is, its introduction into the molecule in general augments the dissociation constant of an acid in a greater degree than methyl, ethyl, &c. It should be noted that all the $\omega\omega'$-disubstituted pimelic acids contain two similar asymmetrical carbon atoms, thus:  $\mathrm{HOOC}-\overset{R}{\underset{H}{C}}-\overset{H}{\underset{H}{\mathrm{C}}}-\overset{H}{\underset{H}{\mathrm{C}}}-\overset{H}{\underset{H}{\mathrm{C}}}-\overset{R}{\underset{H}{C}}-\mathrm{COOH}$, and ought, therefore, according to Van't Hoff's theory, to exist in two inactive isomeric modifications, corresponding to mesotartaric and racemic acids. It is thus possible that the acid measured may not be homogeneous, but may consist of a mixture of the two isomerides; in this case, however, the pairs of isomeric acids must have approximately equal dissociation constants, for otherwise the numbers obtained would vary considerably with the dilution, which is contrary to experiment.

Dimethyl- and diethyl-pentanetetracarboxylic acids are those from which the dimethyl- and diethyl-pimelic acids were prepared by the removal of carbonic anhydride.

These acids each contain two pairs of carboxyl groups united to the same carbon atom. Such close proximity of carboxyl groups greatly increases the strength of an acid; thus, whilst acetic acid has the constant K = 0·00180, the constant of malonic acid is 0·163 (Walden). We consequently find that the constants of dimethyl- and diethyl-pentanetetracarboxylic acids (p. 704) are many times greater than those of the corresponding pimelic acids, the ratios being respectively 100 : 1 and 600 : 1. The ratio between the constants of malonic and acetic acids is 90 : 1. Dimethylpentanetetracarboxylic acid, K = 0·37, may be compared to dimethylmalonic acid, K = 0·076, and diethylpentanecarboxylic acid, K = 2·1, to diethylmalonic acid, K = 0·74. The ratios between the corresponding constants are about 5 : 1 in the one case and 3 : 1 in the other, being thus of the same order.

The fact of the tetracarboxylic acids having four hydrogen atoms which may be split off electrolytically, does not affect the nature of the constant directly. The value obtained is the constant for the first hydrogen atom which is dissociated. From the close proximity of the carboxyl groups, however, the constant is large from the beginning, that is, the first hydrogen atom is considerably dissociated even at small dilutions, so that at moderate dilutions a second hydrogen atom

Dimethylpentanetetracarboxylic Acid,



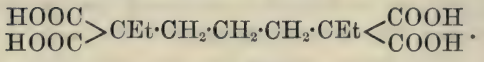
$$\begin{matrix}\mathrm{HOOC}\\\mathrm{HOOC}\end{matrix}\!>\!\mathrm{CMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot CMe}\!<\!\begin{matrix}\mathrm{COOH}\\\mathrm{COOH}\end{matrix}\,.$$

$$\mu_\infty = 350.$$

v.	*μ.*	100*m.*	100*k.*
17·18	77·6	22·2	0·37
34·36	106·0	30·3	0·38
68·7	142·4	40·7	0·40
137·4	187·7	53·6	0·45
275·0	240·5	68·7	0·55

K = 0·37.

Diethylpentanetetracarboxylic Acid,



$$\begin{matrix}\mathrm{HOOC}\\\mathrm{HOOC}\end{matrix}\!>\!\mathrm{CEt\cdot CH_2\cdot CH_2\cdot CH_2\cdot CEt}\!<\!\begin{matrix}\mathrm{COOH}\\\mathrm{COOH}\end{matrix}\,.$$

$$\mu_\infty = 350.$$

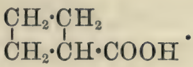
v.	*μ.*	100*m.*	100*k.*
11·3	120·4	34·4	2·3
22·6	163·0	46·6	2·1
45·2	214·0	61·3	2·0
90·4	271·0	77·4	2·2
180·8	334·0	(95·4	6·5)
361·6	402·0	—	—
723·0	468·0	—	—
1446·0	511·0	—	—

K = 2·1.

begins to dissociate, with a corresponding increase of the constant. Thus in the case of the dimethyl acid, after over 40 per cent. of the first hydrogen has been dissociated, the constant rapidly rises. The rise does not take place with the diethyl acid until over 70 per cent. of the first hydrogen is split off, but then the change is very sudden, the value leaping from 2·2 to 6·5.

Polymethylenecarboxylic Acids.

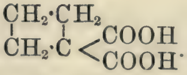
Professor Perkin kindly furnished me with a few carboxyl derivatives of the polymethylenes, in order that they might be compared with the corresponding acids of the saturated series.

Tetramethylenemonocarboxylic Acid, 
$\begin{matrix}CH_2\cdot CH_2 \\ | \quad\ | \\ CH_2\cdot CH\cdot COOH\end{matrix}$.

$\mu_\infty = 356.$

v.	*μ.*	100*m.*	100*k.*
14·5	5·69	1·60	0·00179
29·0	8·08	2·27	0·00182
58·0	11·44	3·21	0·00184
116·0	16·03	4·50	0·00183
232·0	22·4	6·29	0·00182
464·0	31·2	8·77	0·00182
928·0	43·3	12·16	0·00180

K = 0·00182.

α-Tetramethylenedicarboxylic Acid, 
$\begin{matrix}CH_2\cdot CH_2 \\ | \quad\ | \\ CH_2\cdot C\end{matrix}<\begin{matrix}COOH\\ COOH\end{matrix}$.

$\mu_\infty = 353.$

v.	*μ.*	100*m.*	100*k.*
16·5	39·0	11·05	0·0833
33·0	53·8	15·25	0·0832
66·0	73·7	20·9	0·0835
132·0	99·4	28·2	0·0837
264·0	131·5	37·3	0·0838
528·0	168·7	47·8	0·0829
1056·0	215·2	59·5	0·0828

K = 0·0833.

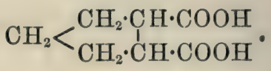
The constant of tetramethylenemonocarboxylic acid, $C_4H_7\cdot COOH$, K = 0·00182, is not far removed from that of valeric acid, $C_4H_9\cdot COOH$, K = 0·00161 (Ostwald); so that the loss of two hydrogen atoms with simultaneous formation of a closed chain does not seem to affect the dissociation constant greatly. The constants of the unsaturated acids having the formula $C_4H_7\cdot COOH$ are: tiglic acid, K = 0·000957, and angelic acid, K = 0·00501.

α-Tetramethylenedicarboxylic acid, $C_4H_6(COOH)_2$, as a derivative of malonic acid (K = 0·163), has a constant (K = 0·083) somewhat smaller than might have been expected. The constants for the corresponding saturated and unsaturated malonic acid derivatives are:—

		K
Propylmalonic acid	$C_4H_8(COOH)_2$....	0·112
Isopropylmalonic acid ..		0·127
Ethylmethylmalonic acid		0·164
Allylmalonic acid, $C_4H_6(COOH)_2$		0·154

all of which are considerably higher than that of the tetramethylene derivative.

β-Pentamethylenedicarboxylic Acid,



$$CH_2<\begin{matrix}CH_2\cdot CH\cdot COOH\\ |\\ CH_2\cdot CH\cdot COOH\end{matrix}.$$

$\mu_\infty = 352.$

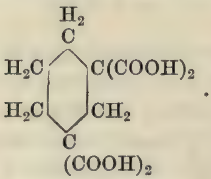
v.	*μ.*	100*m.*	100*k.*
70·75	31·3	8·90	0·0121
141·5	42·9	12·2	0·0120
283·0	58·5	16·6	0·0117
566·0	79·9	22·7	0·0118
1132·0	109·1	31·0	0·0123

K = 0·0120.

This acid may be looked on as a derivative of succinic acid (K = 0·0068). Its constant (K = 0·0120) approximates closely to that of the isomeric allylsuccinic acid, K = 0·0109. The corresponding saturated compounds have the following constants:—

	K.
Propylsuccinic acid	0·0089
Isopropylsuccinic acid	0·0075
Paramethylethylsuccinic acid...	0·0207
Mesomethylethylsuccinic acid...	0·0201

Hexamethylenetetracarboxylic Acid [1 : 1 : 3 : 3],



$\mu_\infty = 350.$

v.	*μ.*	100*m.*	100*k.*
21·25	52·1	14·9	0·123
42·5	72·6	20·7	0·128
85·0	99·3	28·4	0·132
170·0	133·5	38·1	0·138
340·0	175·7	50·2	0·149
680·0	228·6	65·1	0·177

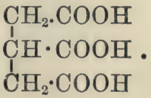
K = 0·12.

It is somewhat singular that the constant of this acid, which contains four carboxyl groups arranged so that it may be regarded as derived from two molecules of malonic acid, should be lower than that of malonic acid itself (K = 0·16). The table shows a steady increase of the constant with increasing dilution. This may be due either to the early dissociation of a second carboxyl hydrogen atom, or to the acid not being perfectly pure.

Tribasic Acids.

As no tribasic acids have hitherto been investigated with respect to their dissociation constants, I have examined the three simplest representatives of the group. For the specimen of tricarballylic acid I have again to thank Professor Perkin.

Tricarballylic Acid,



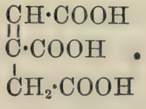
$$\begin{array}{l}\mathrm{CH_2{\cdot}COOH}\\ \;|\\ \mathrm{CH{\cdot}COOH}\,.\\ \;|\\ \mathrm{CH_2{\cdot}COOH}\end{array}$$

$\mu_\infty = 352.$

v.	*μ.*	100*m.*	100*k.*
16·7	20·7	5·87	0·0220
33·4	29·1	8·26	0·0223
66·8	40·4	11·47	0·0222
133·6	55·6	15·80	0·0222
267·0	76·2	21·64	0·0224
534·0	103·0	29·26	0·0227
1068·0	135·8	38·59	0·0226

K = 0·0224.

Aconitic Acid,



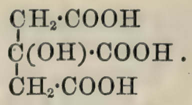
$$\begin{array}{l}\mathrm{CH{\cdot}COOH}\\ \;\|\\ \mathrm{C{\cdot}COOH}\,.\\ \;|\\ \mathrm{CH_2{\cdot}COOH}\end{array}$$

$\mu_\infty = 353.$

v.	*μ.*	100*m.*	100*k.*
28·1	67·0	19·0	0·158
56·2	90·9	25·7	0·158
112·4	120·5	34·1	0·157
224·8	156·0	44·2	0·156
449·6	198·0	56·1	0·159
899·2	249·0	70·5	0·187

K = 0·158.

Citric Acid,



$$\begin{array}{l} CH_2\cdot COOH \\ | \\ C(OH)\cdot COOH \\ | \\ CH_2\cdot COOH \end{array}$$

$$\mu_\infty = 352.$$

v.	μ.	$100m$.	$100k$.
15·17	36·5	10·38	0·0793
30·35	50·7	14·40	0·0800
60·7	69·4	19·7	0·0798
121·4	94·2	26·7	0·0804
243·0	124·6	35·4	0·0798
486·0	162·0	46·0	0·0807
972·0	205·6	58·5	0·0850
1944·0	254·5	72·3	0·0971

$$K = 0·0800.$$

Tricarballylic, citric, and aconitic acids bear the same relation to each other, with respect to their constitution, as do succinic, malic, and fumaric (or maleïc) acids. We should consequently expect a parallelism in the values of the dissociation constants of the three series. The following table shows that this parallelism actually exists :—

Acid.	K.	Acid.	K.
Succinic.............	0·0068	Tricarballylic........	0·0224
Malic	0·0395	Citric................	0·0800
Fumaric.............	0·093	Aconite	0·158
Maleïc	1·17		

First in point of strength come the unsaturated acids, next, the hydrogen acids, and lastly, the saturated parent acids.

Corresponding with the greater number of carboxyl groups in the tribasic acids, the constants are greater than those of the bibasic acids.

The dissociation of the second hydrogen atom begins when the degree of dissociation of the first is 56 per cent. in the case of aconitic acid, and 46 per cent. in the case of citric acid.

Alkyl Hydrogen Salts of Bibasic Acids.

Very few of the alkyl hydrogen salts of bibasic organic acids have hitherto been prepared in the pure state. This is partly owing to the difficulty of obtaining them free from admixture of the dihydrogen and the dialkyl salts, and partly to the want of interest attaching to them. Now, however, that the alkyl potassium salts form the starting point for the electrolytic synthesis of bibasic acids (Crum Brown and Walker, *Annalen*, **261**, 107), the properties of the acid ethereal salts from which these potassium salts are derived have become of greater importance. Most of the alkyl hydrogen salts hitherto obtained have merely occurred as secondary products in the preparation of the dialkyl salts by direct etherification of the bibasic acids, although one or two have been prepared in other ways.

There are two methods, one general and one special, by which the alkyl hydrogen salts may be prepared. The general method is the half saponification of the corresponding dialkyl salt; the special method is the direct addition of an alcohol to the anhydride of the bibasic acid, if it should form one.

If proper precautions are taken, the method of half saponification seems universally applicable. The saponification is effected by means of alcoholic solution of potash. In preparing ethyl potassium succinate, for example, 1 mol. of diethyl succinate is dissolved in three or four times its volume of alcohol, and to the solution, 1 mol. of potassium hydroxide also dissolved in alcohol is gradually added. The reaction takes place according to the equation

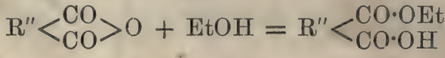
$$\mathrm{EtOOC{\cdot}CH_2{\cdot}CH_2{\cdot}COOEt + KOH = EtOOC{\cdot}CH_2{\cdot}CH_2{\cdot}COOK + EtOH.}$$

A portion of the ethyl potassium salt begins to separate out at once. After standing over night, the semi-solid mass is allowed to digest for some time at a moderate heat, and then the alcohol is distilled off. The residue is treated with water, which dissolves the potassium ethyl salt, whilst a layer of unattacked dialkyl salt floats to the top of the aqueous solution. The ethereal salt is removed by shaking up with ether, and separating. In the aqueous solution there is, besides the ethyl potassium salt, a small quantity of the dipotassium salt. The separation of these substances from each other may be effected in two ways. First, advantage may be taken of the relatively great solubility of the ethyl potassium salts of bibasic acids in absolute alcohol, the dipotassium salts being practically insoluble in this medium. Or, second, the separation may be effected by converting the potassium salts into the barium salts; the ethyl barium salts are for the most part easily soluble in water, whilst the normal barium salts are only very slightly soluble. If the first method is adopted, the dry potassium salts are treated with boiling alcohol in a fat-extraction apparatus. The alcoholic solution of the ethyl potassium salt is evaporated to dryness, the residue then dissolved in water, acidified, and the acid extracted with ether. The ethereal solution is washed with a little water and the ether distilled off. Practically pure ethyl hydrogen succinate remains.

Should the purification by means of the barium salts be preferred, the neutral solution of the potassium salts is treated with barium chloride, which precipitates almost all the normal barium salt, and leaves the barium ethyl salt in solution. Or the crude acid may be liberated from the potassium salt, and boiled with water and barium carbonate until the solution is neutral. The filtrate in both cases is treated with acid and extracted with ether, as in the alcohol method of separation. If a perfectly pure product is wanted, it is often advisable to apply the two methods of purification in succession.

In some cases, the method of half-saponification as above described does not yield a satisfactory result. For example, the diethyl salts of dialkylmalonic acids, when treated in this way, give scarcely any ethyl potassium salt, half of the diethyl salt being fully saponified, whilst the other half remains untouched. With such substances it is necessary to carry out the saponification in several stages. The dialkyl salt is dissolved in at least 20 times its weight of alcohol not quite absolute—about 95 per cent. This solution is cooled to 0°, and to it is added a dilute alcoholic solution of caustic potash, also at 0°. The quantity of potash taken should not exceed one-fourth of the quantity necessary for half saponification of the dialkyl salt. No precipitate should separate out on standing or on subsequent boiling. The alcohol is distilled off, and may be used for dissolving the dialkyl salt recovered. The residue is treated with water, the ethereal layer removed, and the aqueous solution worked up as before. The ethyl potassium salts obtained directly in this way are very nearly pure.

Acids, such as maleïc acid or phthalic acid, of which the anhydrides are easily obtainable, may be readily converted into ethyl hydrogen salts by boiling the anhydride for about half an hour with a considerable excess of ethyl alcohol. Direct addition takes place according to the following equation:—



$$\mathrm{R}''<^{\mathrm{CO}}_{\mathrm{CO}}>\mathrm{O} + \mathrm{EtOH} = \mathrm{R}''<^{\mathrm{CO{\cdot}OEt}}_{\mathrm{CO{\cdot}OH}}.$$

The purification may be effected by any of the methods previously described.

The ethyl hydrogen salts of bibasic acids resemble very much in their behaviour the monobasic acids from which they may be supposed to be derived by the substitution of the group COOEt for an atom of hydrogen. The lower members of the series are liquid at the ordinary temperature, and have a pleasant acid smell when hot. They may be distilled under reduced pressure with little or no decomposition. Their solubility in cold water is in general much the same as that of the dihydrogen salt from which they are produced. In alcohol and in ether they are easily soluble. Their alkaline salts are very soluble in water (1 part of which dissolves from 2 to 4 parts of salt), and are also moderately soluble in alcohol. These salts may be precipitated from alcoholic solution by the addition of ether, and, when obtained in this way, are sometimes liquid, although they usually solidify on standing. The calcium and barium salts are fairly soluble in water, the degree of solubility corresponding roughly to that of the salts of the monobasic acids from which they are derived.

The alkaline salts, when boiled for a long time with water, suffer partial decomposition into the di-metallic salt and the diethyl salt. The amount of decomposition differs in the various cases, but is never very great, so that in general an aqueous solution of the salt may be evaporated to dryness without any considerable loss.

The methyl hydrogen salts resemble the ethyl hydrogen salts in every particular, the chief difference being that they crystallise more easily and melt at a higher temperature.

As the chief impurity to be feared in the substances examined as to their electrical conductivity was the corresponding dihydrogen salt, a weighed quantity of the alkyl hydrogen compound was always titrated with a standard solution of baryta (phenolphthaleïn being used as indicator), in order to test its freedom from the bibasic acid. The strengths of the solutions employed were also determined by titration.

Ethyl Hydrogen Malonate, $EtOOC{\cdot}CH_2{\cdot}COOH$.

$\mu_\infty = 356.$

v.	μ.	$100m$.	$100k$.
8·57	21·5	6·04	0·0454
17·14	30·3	8·52	0·0464
34·28	41·9	11·8	0·0458
68·56	57·3	16·1	0·0451
137·1	77·9	21·9	0·0447
274·2	104·1	29·3	0·0441

K = 0·0451.

Ethyl Hydrogen Succinate, $EtOOC{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.

$\mu_\infty = 352.$

v.	μ.	$100m$.	$100k$.
18·2	8·13	2·31	0·00300
36·4	11·50	3·27	0·00303
72·8	16·20	4·60	0·00304
145·6	22·7	6·45	0·00304
291·0	31·3	8·90	0·00299
582·0	43·5	12·36	0·00300

K = 0·00302.

Ethyl Hydrogen Isosuccinate, EtOOC·CHMe·COOH.

$\mu_\infty = 352.$

v.	*μ.*	100*m.*	130*k.*
17·0	27·6	7·83	0·0390
34·0	38·3	10·88	0·0390
68·0	52·6	14·95	0·0391
136·0	72·0	20·4	0·0387
272·0	97·1	27·6	0·0387
544·0	127·8	36·3	0·0381

K = 0·0387

Ethyl Hydrogen Dimethylmalonate, $\mathrm{EtOOC{\cdot}CMe_2{\cdot}COOH}$.

$\mu_\infty = 352.$

v.	*μ.*	100*m.*	100*k.*
44·0	38·9	11·05	0·0312
88·0	53·6	15·22	0·0310
176·0	72·5	20·6	0·0304
352·0	96·5	27·4	0·0294
704·0	128·1	36·4	0·0296
1408·0	167·5	47·6	0·0307

K = 0·0304.

Ethyl Hydrogen Ethylmalonate, EtOOC·CHEt·COOH.

$\mu_\infty = 352.$

v.	*μ.*	100*m.*	100*k.*
33·75	39·5	11·04	0·0405
67·5	53·6	15·22	0·0405
135·0	72·9	20·7	0·0400
270·0	97·9	27·8	0·0397
540·0	129·9	36·9	0·0400
1080·0	167·9	47·7	0·0402

K = 0·0401.

Ethyl Hydrogen Adipate, $\mathrm{EtOOC{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH}$.

$\mu_\infty = 351.$

v.	*μ.*	100*m.*	100*k.*
93·0	17·3	4·93	0·0027
186·0	23·7	6·75	0·0026
372·0	32·1	9·15	0·0025
744·0	43·0	12·25	0·0023
1488·0	57·1	16·27	0·0021

K = 0·0025 (?).

I did not succeed in obtaining ethyl hydrogen adipate entirely free from impurity, which accounts for the continual fall in the value of *k*.

Ethyl Hydrogen Diethylmalonate, $EtOOC \cdot CEt_2 \cdot COOH$.

$\mu_\infty = 351.$

v.	*μ*.	100*m*.	100*k*.
36·5	30·9	8·83	0·0235
73·0	42·7	12·2	0·0233
146·0	58·7	16·8	0·0231
292·0	79·9	22·8	0·0231
584·0	106·8	30·5	0·0230
1168·0	140·0	40·0	0·0228

K = 0·0231.

Ethyl Hydrogen Suberate, $EtOOC \cdot [CH_2]_6 \cdot COOH$.

This substance when pure is an oil which solidifies at low temperatures to a mass of colourless crystals melting at 18°.

$\mu_\infty = 351.$

v.	*μ*.	100*m*.	100*k*.
74·5	11·5	3·28	0·00148
149·0	16·0	4·57	0·00146
298·0	22·3	6·35	0·00145
596·0	31·3	8·92	0·00147
1192·0	43·3	12·34	0·00146

K = 0·00146.

Ethyl Hydrogen Sebate, $EtOOC \cdot [CH_2]_8 \cdot COOH$.

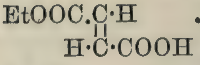
Rowney (*J. Chem. Soc.*, **4**, 334) noticed that this substance was formed in the preparation of diethyl sebate from sebacic acid, but was unable to isolate it. Neison (*ibid.*, **29**, 219) obtained it in the same way, but states that he could not purify it on account of the readiness with which it and its salts split up into the diethyl ether and the acid or normal salt of the acid. The substance he obtained was an oil which crystallised at 10° in snow-white needles. It is true that ethyl hydrogen sebate and its alkaline salts do decompose to some extent, as Neison states, but not more so than the corresponding compounds of other bibasic acids, and it is a matter of no great difficulty to obtain the ethyl hydrogen salt practically pure. The melting point of the pure substance is 38°.

$\mu_\infty = 350.$

v.	μ.	$100m$.	$100k$.
483·0	28·1	8·03	0·00144
966·0	38·8	11·08	0·00143
1932·0	53·6	15·31	0·00143

$K = 0{\cdot}00143.$

Ethyl Hydrogen Fumarate,



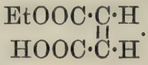
$$\begin{array}{r}\text{EtOOC.C·H}\\ \|\ \ \ \ \ \\ \text{H·C·COOH}\end{array}.$$

$\mu_\infty = 354.$

v.	μ.	$100m$.	$100k$.
22·0	34·5	9·76	0·0480
44·0	47·7	13·5	0·0477
88·0	65·3	18·4	0·0474
176·0	88·0	24·9	0·0468
352·0	117·3	33·1	0·0468
704·0	153·2	43·3	0·0469

$K = 0{\cdot}0473.$

Ethyl Hydrogen Maleate,



$$\begin{array}{l}\text{EtOOC·C·H}\\ \qquad\quad\ \|\\ \text{HOOC·C·H}\end{array}.$$

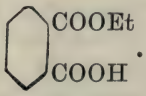
$\mu_\infty = 354.$

v.	μ.	$100m$.	$100k$.
51·0	74·9	21·1	0·111
102·0	100·3	28·3	0·110
204·0	132·2	37·3	0·109
408·0	170·7	48·2	0·110
816·0	212·0	59·9	0·110

$K = 0{\cdot}110.$

I am indebted to Dr. J. Shields for the specimens of the two foregoing unsaturated substances, which he has described in Trans., 1891, **59**, 736.

Hydrogen Ethyl Phthalate,



$\mu = 352.$

v.	μ.	$100m$.	$100k$.
120·0	79·9	22·7	0·0555
240·0	107·0	30·4	0·0553
480·0	140·0	39·8	0·0556
960·0	179·0	50·8	0·0548
1920·0	221·0	62·8	0·0540

$K = 0{\cdot}0551.$

The following table embodies the results obtained for the ethyl hydrogen salts, and, for the sake of comparison, the constants of the corresponding dihydrogen salts have been added:—

Acid.	Dihydrogen salt. K.	Ethyl hydrogen salt. K.	Ratio.
Malonic	0·163	0·0451	3·6 : 1
Succinic	0·0068	0·00302	2·3 : 1
Adipic	0·00365	0·0025 (?)	1·3 : 1
Suberic	0·00296	0·00146	2·0 : 1
Sebacic	0·00276	0·00143	1·9 : 1
Methylmalonic	0·086	0·0387	2·2 : 1
Ethylmalonic	0·127	0·0401	3·2 : 1
Dimethylmalonic	0·076	0·0304	2·5 : 1
Diethylmalonic	0·74	0·0231	32·0 : 1
Fumaric	0·093	0·0473	2·0 : 1
Maleïc	1·17	0·110	10·6 : 1
Phthalic	0·121	0·0551	2·2 : 1

It is evident from the table that the constant of the dihydrogen salts is in general from 2 to 2·5 times as great as the constant of the corresponding ethyl hydrogen salts. The only exceptions to this rule are formed by the bibasic acids, the constants of which are very high, greater than 0·1.

The bibasic acids are always stronger than the monobasic acid from which they are derived by the substitution of the group carboxyl for a hydrogen atom. This is owing to the effect of one carboxyl group on the other. Carboxyl, in virtue of its acid character, increases the dissociation of the hydrogen of a carboxyl group contained in the same molecule as itself, and this increase of the dissociation is the greater the more nearly the carboxyl groups occur together in the molecule. For example, the constant of succinic acid is 0·0068, whilst that of the isomeric methylmalonic acid is 0·086, more than 12 times as great. In the first case, the carboxyl groups are separated by two carbon atoms; in the second case, they are both attached to the same carbon atom. Problems of geometrical isomerism may be attacked with some success from this side. The fact of the constant of maleïc acid being more than 12 times greater than the constant of fumaric acid indicates closer approximation of the carboxyl group in the former than in the latter, a conclusion which corresponds with the ready formation of maleïc anhydride. The influence of the introduction of various alkyl radicles into the molecule of malonic and succinic acids has been discussed from this point of view by Bethmann (*loc. cit.*) and by Walden (*loc. cit.*). One carboxyl group greatly affects the dissociation of another when the two are close together, but the effect diminishes rapidly as the distance between the two increases. The same thing is observed in the case of the carboxethyl group, only the limits of the influence are much narrower. The group carboxethyl has a distinctly acid character, but the effect of its introduction into an acid molecule is practically *nil* when it is far removed from the carboxyl group. Thus the constants of ethyl hydrogen suberate (K = 0·00146) and sebate (K = 0·00143) are nearly the same as those of high members of the series of saturated monobasic acids, for example, caproic acid (K = 0·00145). When the carboxethyl and carboxyl groups are near each other in the molecule, the influence is much more marked; but it does not amount to that exercised by a second carboxyl group, nor does it seem to be proportional to this. The want of proportionality may be accounted for either directly from the nature of the influence exerted by the different groups, or it may be that the substitution of the ethyl group for a hydrogen atom in a carboxyl group increases the distance between this group and a second carboxyl to which it was closely neighboured. The ratio between the greatest and least of the constants of the dihydrogen salts in the table is 400 to 1; the corresponding ratio for the ethyl hydrogen salts is only 77 to 1. This shows the smaller range of influence of the carboxethyl group when compared with the carboxyl group. It is only in the very strong acids, however, that there is any striking difference in the effect of the two substituents.

In addition to the above ethyl hydrogen salts, I have examined methyl hydrogen succinate and methyl hydrogen phthalate, in order to obtain an idea of the relative acidity of the groups COOEt and COOMe.

Methyl Hydrogen Succinate, $MeOOC\cdot CH_2\cdot CH_2\cdot COOH$.

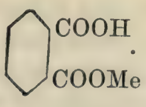
This substance crystallises from benzene in hard, colourless plates. Its melting point is 58°.

$\mu_\infty = 845.$

v.	μ.	$100m$.	$100k$.
19·4	8·72	2·46	0·00321
38·8	12·41	3·50	0·00328
77·6	17·4	4·91	0·00327
155·2	24·3	6·87	0·00327
310·4	33·9	9·57	0·00326
620·8	46·9	13·23	0·00326

K = 0·00326.

Methyl Hydrogen Phthalate,



This acid ethereal salt crystallises from benzene in rosettes of hard, glistening needles. Its melting point is 82·5°.

$\mu_\infty = 352.$

v.	*μ*.	100*m*.	100*k*.
102	79·9	22·7	0·0653
204	107·4	30·5	0·0656
408	141·1	40·1	0·0658
816	180·2	51·2	0·0658

K = 0·0656.

The constants of the methyl hydrogen salts are thus somewhat greater than those of the corresponding ethyl hydrogen salts, as the following table indicates:—

Acid.	Ethyl hydrogen salt.	Methyl hydrogen salt.
Succinic........	0·00302	0·00326
Phthalic	0·0551	0·0656

The group COOMe therefore gives the molecule into which it is introduced a more acid character than does the group COOEt, although the difference between their acidifying effects is not great.

LXII.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF EDINBURGH.

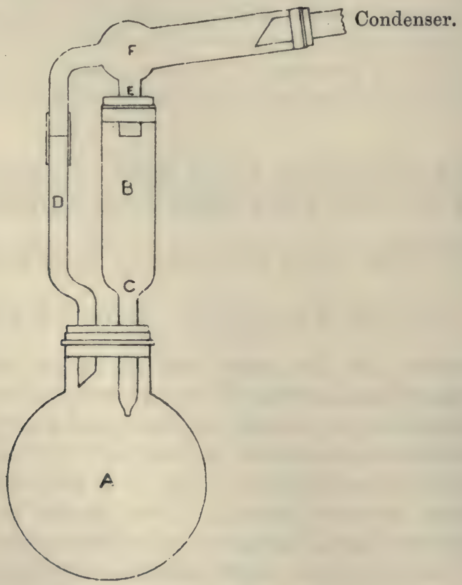
No. VIII. *On the Preparation of Alkyl Iodides.*

By James Walker, D.Sc., Ph.D., F.R.S.E.

The alkyl iodides are universally obtained by the interaction of an alcohol and phosphorus iodide. It is not customary to prepare a pure iodide of phosphorus beforehand, but simply to allow phosphorus and iodine to interact in presence of the alcohol. The only objection to this method in its usual form is that it is somewhat tedious, and requires pretty constant attention. This is due to the fact that yellow phosphorus cannot be used conveniently in the preparation, as the action between it and solid iodine is too vigorous. If it is employed at all, the iodine must be previously dissolved in the alcohol, which, in most cases, necessitates the use of quantities of the latter much larger than are actually required. The excess of alcohol is often difficult to get rid of without some loss of the alkyl iodide formed. Even in this case, however, the materials cannot be mixed all at once, but the yellow phosphorus must be added to the solution in successive small pieces.

The action between red phosphorus and solid iodine in presence of an alcohol is much more moderate, so that the solids may be brought into contact in small quantities at a time without risk. In the preparation of ethyl iodide, however, it takes from an hour to an hour and a half to add 100 grams of iodine to the requisite quantity of alcohol and amorphous phosphorus. When 500 to 1000 grams of iodine have thus to be worked up into alkyl iodide, this slow addition becomes extremely irksome.

Having of late had occasion to prepare large quantities of ethyl and methyl iodides, I sought for some means of lightening the labour and doing away with the attention involved in the above modes of preparation, and, after numerous experiments, arrived at the following plan, which works very well in practice, requiring little supervision, and shortening the time expended to about a third. A sketch of the apparatus employed is given below. We will suppose that the preparation is to be somewhat over 550 grams of ethyl iodide.



The materials required are—

500	grams of	iodine.
250	,,	ethyl alcohol.
30	,,	yellow phosphorus.
30	,,	red phosphorus.

The alcohol and the two varieties of phosphorus are introduced into the wide-necked, round-bottomed flask A, of about 1 litre capacity. Into this flask, by means of a double-bored cork, are fitted an adapter B, and a wide glass tube D. The narrow tube of the adapter is drawn out at the end, as indicated in the figure, until only a small opening is left. At C the adapter is loosely plugged with glass wool, and into it 100 grams of iodine are filled and packed down tightly. A glass ┌┬-piece, F, completes the connection, one limb of this being inserted through a cork in the adapter, another being connected with the tube D by means of india-rubber tubing. A wide reflux condenser is attached by means of a cork to the remaining limb. The top-piece of a Drechsler fat-extraction apparatus answers very well for making this three-fold connection, and it is figured in the sketch. The apparatus being thus fitted up, and the joints proved to be tight, the flask is placed on a water-bath, and the alcohol in it boiled. As bumping frequently occurs, it is well to add a few fragments of porous tile to the contents of the flask.

The vapour from the boiling alcohol passes up the tube D, and is condensed in the condenser, the liquid dropping down through E on to the iodine. As the alcohol proceeds downward, it becomes saturated with iodine, and when it falls back into A the reaction begins. The narrow end of the adapter ought to be at a lower level than the end of the tube D, in order to be kept hot by the alcohol vapour, for otherwise iodine may crystallise out from the alcohol solution as it runs down, and block up the narrow opening of the tube. D should be at least 6—8 mm. in bore to allow free passage to the vapour. The distillation should not be allowed to proceed too rapidly, for a considerable amount of heat is disengaged during the interaction in the liquid, which causes rapid ebullition, and this, from more and more iodine being dissolved and carried into the flask, always tends to increase. The liquid should not, in general, be allowed to run in a continuous stream from E, but only in a rapid succession of drops. When all the iodine has been dissolved, the heating is continued until there is no longer any coloration of the liquid due to iodine. The flask is then cooled by a stream of cold water, and a fresh charge of iodine introduced into B. The heating is recommenced, and the series of operations repeated until the whole 500 grams of iodine have been worked up.

As the reaction proceeds and ethyl iodide accumulates in the liquid, less and less heat is required to keep the distillation going. This is due, not only to ethyl iodide being more volatile than alcohol, but also to the iodine being much more soluble in the former than in the latter; so that, for a given amount of liquid running back into B, more iodine is dissolved in the later stages of operation than at the beginning, which, of course, causes a greater evolution of heat. The first 100 grams of iodine take about 25 minutes to dissolve; the time falls to about 15 minutes for the last 100 grams. After a little experience in regulating the heating has been obtained, the apparatus may be safely left to itself during the working up of each charge of iodine. If the last charge is introduced too rapidly, a quantity of a white solid, probably a phosphonium iodide, appears on the walls of the upper portions of the apparatus. The mixture of the two varieties of phosphorus in equal proportions attacks the iodine more rapidly than either variety singly. This is very likely due to some difference in the state of division of the phosphorus produced during the ebullition.

When the reaction is completed, a small quantity of water is poured down the condenser to destroy any phosphonium compounds which may be formed. The flask is then detached, and the liquid distilled off on the water-bath. The distillate, after being washed with water, separated from the aqueous layer, and dried, is practically pure ethyl iodide. The average yield of refractionated ethyl iodide from 500 grams of iodine is 570 grams, or 93 per cent. of the theoretical quantity.

Methyl iodide may be prepared in precisely the same way, methyl alcohol being substituted for ethyl alcohol. As both the methyl compounds are more volatile than the corresponding ethyl compounds, less heat is required to keep the action going. In fact, during the addition of the last charges of iodine, external heating may be almost dispensed with when once the action is started. The reflux condenser in this case must be a very efficient one. The yield of methyl iodide is somewhat greater than the quantity of iodine taken.

In order to ascertain if the above method of preparation is applicable to higher members in the series, an experiment was made with isobutyl alcohol. Here a sand-bath must be used instead of a water-bath. In this case, too, the iodide boils at a higher temperature than the alcohol. As the alcohol is only slightly soluble in water, no excess of it was taken, but just the quantity equivalent to the iodine employed. The action in its later stages was inclined to be rather violent, considerable quantities of hydrogen iodide being evolved, unless the distillation was well regulated. After all the iodine had disappeared, the product was distilled with steam. The heavy layer of iodide in the distillate was separated from the aqueous layer, dried, and fractionated. 250 grams of iodine yielded 300 grams of isobutyl iodide.

The chief precaution to be taken in the above preparations is the proper regulation of the temperature while the final charge is being introduced. The tendency is always to supply too much heat to the liquid; so that, until some experience in the method has been gained, it is advisable to conduct the distillation during the last stages very slowly. The iodine should not be added in quantities of over 100 grams at a time. If this limit is not exceeded, no serious loss takes place, even although the ebullition happen by mischance to proceed too rapidly.

The product obtained by the use of yellow phosphorus always seems to contain small quantities of a phosphorus compound, as may be detected by the smell. The presence of this substance, however, is by no means a disadvantage for many purposes; the iodides thus prepared keep much longer without separation of iodine than the iodides obtained from amorphous phosphorus alone, and in synthetical operations, such as the production of substituted malonic ethers, give a much cleaner product.

LXIII.—*Production of Pyridine Derivatives from the Lactone of Triacetic Acid.*

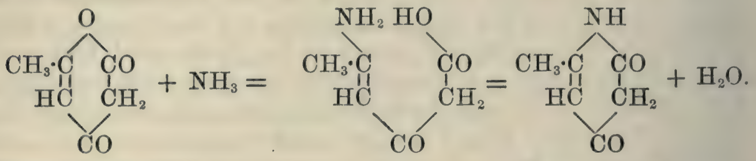
By N. Collie, PhD., F.R.S.E., and W. S. Myers, B.Sc., University College, London.

It has been long known that such substances as ethyl acetoacetate and dehydracetic acid, when treated with ammonia, yield pyridine derivatives. It was therefore expected that triacetic lactone, when treated in a similar manner, would no doubt also give a closed ring compound containing nitrogen.

That the triacetic lactone probably does yield such a compound when warmed with strong solution of ammonia has already been pointed out by one of us (Trans., 1891, **59**, 617), but the nature and constitution of the new compound was not then investigated. This compound was shown to be formed by a simple reaction:—

$$C_6H_6O_3 + NH_3 = C_6H_7NO_2 + H_2O.$$

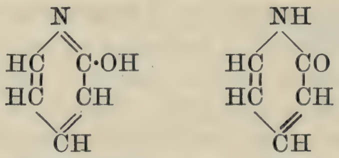
If the action of the ammonia on triacetic lactone be similar to that which occurs when such substances as dimethylpyrone or coumalinic acid are warmed with ammonia, then the reaction could be expressed as follows:—



Triacetic lactone. New compound.

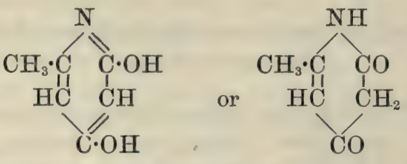
That the reaction does occur in the above manner is rendered highly probable by the results we have obtained.

Von Pechmann has shown (*Ber.*, **24**, 3144—3153) that tautomerism undoubtedly exists in these oxygenated pyridine derivatives, and that the hydroxypyridines behave both as hydroxy-derivatives and also as compounds where the hydrogen atom of the hydroxyl group shifts to the nitrogen atom.



Hydroxypyridine. Pyridone.

The compound which we have obtained from triacetic lactone might have, therefore, either of the two following formulæ:—



and we therefore propose to call it the $\alpha_1\gamma$-*dihydroxy-α-picoline*. When it is treated with bromine, a dibromide is obtained:—

$$C_6H_7NO_2 + Br_2 = C_6H_7NO_2{\cdot}Br_2.$$

Various attempts were made to displace the oxygen by chlorine, and at first without success. If the substance is dissolved in phosphorus oxychloride, but pentachloride of phosphorus added, the reaction is very violent, and the only product which could be obtained was a very small quantity of a monochloride:—

$$C_6H_7NO_2 + PCl_5 = C_6H_6{\cdot}NOCl + HCl + POCl_3.$$

Eventually, however, it was found that if oxychloride of phosphorus alone was used a dichloride was produced :—

$$3C_6H_7NO_2 + 2POCl_3 = 3C_6H_5NCl_2 + 2H_3PO_4.$$

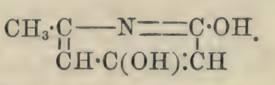
This dichloride possessed all the properties of a dichloropicoline, a sweet, pleasant smell, very feeble basic properties, forming an unstable double salt with chloride of platinum ; whilst, when it was passed, together with hydrogen, through a tube filled with zinc-dust and heated to a low red heat, a considerable quantity of α-picoline, b. p. 128—129°, was obtained :—

$$C_6H_5NCl_2 + 2H_2 = C_6H_7N + 2HCl.$$

This proves that the original substance contains a methyl group in the α-position relatively to the nitrogen atom. The α-picoline, when oxidised with permanganate of potash solution, gave picolinic acid ; the platinum, gold, and picric acid double salts were also prepared, but the melting points were found to be considerably higher than those noticed by former workers. In order to be certain that we were really dealing with α-picoline, considerable trouble was taken to prepare that substance in a pure state by other known methods :—(1.) It was prepared by heating the methiodide of pyridine. This picoline gave with platinic chloride, gold chloride, and picric acid, salts with identically the same melting points and the same crystalline form as those obtained from the picoline we had prepared from the triacetic lactone. (2.) The melting points of the platinum, gold, and picric acid salts, prepared from the fraction boiling between 128° and 129° of the bases from bone oil, although not quite identical with those of the salts already prepared, were not very much lower, and certainly much higher than those given by Ladenburg and Lange.

EXPERIMENTAL PART.

α′γ-Dihydroxy-α-picoline,



$$\begin{array}{l} CH_3\cdot C\text{——}N\text{==}C\cdot OH. \\ \quad\; \| \qquad\qquad\qquad\; | \\ \quad CH\cdot C(OH){:}CH \end{array}$$

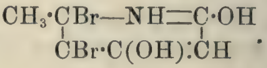
The preparation and properties of this substance have been already shortly described (*loc. cit.*). We have found that, even after prolonged treatment with strong ammonia, the yield is never theoretical, and that usually only 60 to 70 per cent. of the proper amount is obtained. For instance, 55 grams of the triacetic lactone gave 37 grams of the new compound.

During the purification of the crude dihydroxypicoline, by recrystallisation from very dilute acetic acid, we noticed that, on evaporation of the mother liquors, an insoluble substance always separated in flocks having a deep blue colour. This substance resembles indigo in a most remarkable manner. It is quite insoluble in all ordinary reagents. We found that pure phenol dissolved it, when hot, to a slight extent. It is changed to a nearly colourless, pink compound when treated with strong reducing agents, but, on exposure to the air for a few seconds, the original blue substance is re-formed. Unlike indigo, it is not volatile. Unforturately we have been quite unable to collect any large quantity of it, and owing to its great insolubility we were not able to purify it, and so are ignorant of its composition. It is always formed when the crude lactone is used, but, when pure triacetic lactone is treated with ammonia, not a trace of the blue compound could be obtained.

It is, therefore, no doubt produced from some bye-product formed, together with the triacetic lactone, by the action of sulphuric acid on dehydracetic acid.

The prolonged action of nascent hydrogen produced from tin and hydrochloric acid was without action on the dihydroxypicoline, as even after several days action nearly the whole of the dihydroxypicoline was recovered unchanged. The oxidation by means of permanganate of potash was also tried, a very violent reaction occurring when permanganate of potash is added to a warm solution of dihydroxypicoline. A crystalline potassium salt was eventually obtained, but neither it nor the acid could be prepared in a state fit for analysis, so this investigation was not carried further. The dihydroxypicoline was also heated for several hours at 150° with acetyl chloride, but without result.

Dihydroxypicoline dibromide,



$$\begin{array}{l} CH_3\cdot CBr—NH{=}C\cdot OH \\ \;\;\;\;\;\;\;| \qquad\qquad\quad | \\ \;\;\;\;\;\; CBr\cdot C(OH){:}CH \end{array}.$$

When 5 grams of the dihydroxypicoline was dissolved in strong acetic acid, and 6·4 grams of bromine carefully added, the solution became warm. On cooling, about 8 grams of a granular salt separated. This was collected and recrystallised from hot acetic acid. It was eventually obtained in the form of white needles melting about 220° (226° corr.) with much blackening and charring. On analysis, the following numbers were obtained :—

Water of Crystallisation.

1·5525 gram of salt lost 0·1740 gram H_2O at 130° = 11·20 per cent. H_2O ; calculated for $C_6H_7NO_2Br_2,2H_2O$ = 11·21 per cent. H_2O.

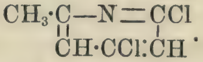
Analysis of Dry Salt.

I. 0·2080 gram of salt gave 0·2000 gram CO_2 and 0·0392 gram H_2O.
II. 0·2255 gram of salt gave 0·2140 gram CO_2 and 0·0425 gram H_2O.
III. 0·3023 gram of salt gave 13·8 c.c. N at 15° and 767 mm.
IV. 0·2848 gram of salt gave 12·8 c.c. N at 16·5° and 767 mm.
V. 0·350 gram of salt gave 0·4640 gram AgBr.

	Calculated for $C_6H_7NO_2Br_2$.	Found.				
		I.	II.	III.	IV.	V.
C....	25·26	26·22	25·85	—	—	—
H....	2·46	2·09	2·09	—	—	—
N....	4·91	—	—	5·39	5·27	—
Br ..	56·15	—	—	—	—	56·41

The substance, therefore, is dihydroxypicoline dibromide.

Dichloropicoline,



$$\begin{array}{l} CH_3\cdot C—N═CCl \\ \quad\;\; \| \qquad\quad | \\ \quad\; CH\cdot CCl:CH \end{array}.$$

10 grams of the dihydroxypicoline was dissolved in phosphorus oxychloride, and 17 grams of phosphorus pentachloride added little by little, the temperature being kept at about 130° by means of an oil-bath. The excess of phosphorus oxychloride was then distilled off, and the pale yellow liquid left in the flask treated with water; on blowing steam through the mixture, a small quantity of an oil distilled over with the water, and from the residue about 3 grams of a crystalline compound was obtained containing chlorine. The reaction, therefore, did not seem to be a simple one, and after several experiments, only a very small amount of the oil and of the solid could be obtained. The solid, after repeated crystallisation from alcohol, melted at 170—172° (173—175° corr.), and on analysis the substance, dried at 130°, gave the following figures:—

I. 0·0823 gram of substance gave 0·1515 gram CO_2 and 0·0356 gram H_2O.
II. 0·2311 gram of substance gave 0·4296 gram CO_2 and 0·0932 gram H_2O.
III. 0·2757 gram of substance gave 22·5 c.c. N at 15° and 754·8 mm.
IV. 0·1087 gram of substance gave 9·0 c.c. N at 15° and 758 mm.
V. 0·1870 gram of substance gave 0·187 AgCl.

	Calculated for	Found.				
	C_6H_6NOCl.	I.	II.	III.	IV.	V.
C....	50·18	50·20	50·70	—	—	—
H....	4·18	4·81	4·48	—	—	—
N....	9·75	—	—	9·50	9·67	—
Cl ..	24·73	—	—	—	—	24·73

A determination of the water of crystallisation gave the following results :—

I. 0·3459 gram of substance lost 0·0392 gram H_2O = 11·34 per cent. H_2O.

II. 0·7231 gram of substance lost 0·0814 gram H_2O = 11·26 per cent. H_2O.

Calculated for $C_6H_6NOClH_2O$ = 11·15 per cent. H_2O.

That a monochloride should be formed in presence of a large excess of phosphorus pentachloride is not easy to explain, for we afterwards found that the oil which is produced at the same time as the monochloride was *dichloropicoline*, and that the only practical method for its manufacture was by boiling dihydroxypicoline with *phosphorus oxychloride alone.*

After many experiments had been tried with phosphorus pentachloride and dihydroxypicoline and a very large amount of the latter substance wasted, we tried the prolonged action of phosphorus oxychloride alone, and at once obtained a large quantity of the liquid dichloropicoline. It was carefully fractionated and boiled at 200—201° (205—206° corr.).

I. 0·1718 gram of substance gave 0·2797 gram CO_2 and 0·0591 gram H_2O.

II. 0·1665 gram of substance gave 0·2701 gram CO_2 and 0·0544 gram H_2O.

III. 0·1329 gram of substance gave 0·2170 gram CO_2 and 0·0443 gram H_2O.

IV. 0·3785 gram of substance gave 0·6740 gram AgCl.

V. 0·2770 gram of substance gave 0·4920 gram AgCl.

VI. 0·1735 gram of substance gave 13·0 c.c. N at 8° and 754 mm.

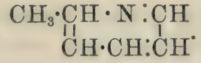
	Calculated for	Found.					
	$C_6H_5NCl_2$.	I.	II.	III.	IV.	V.	VI.
C....	44·44	44·40	44·24	44·53	—	—	—
H....	3·09	3·82	3·63	3·70	—	—	—
N....	8·64	—	—	—	—	—	8·98
Cl ..	43·82	—	—	—	44·11	43·85	„

Dichloropicoline is an oil which does not mix with water. It dissolves in strong hydrochloric acid, but is reprecipitated again on dilution. The strong hydrochloric acid solution gives an insoluble double salt with platinum chloride, which was prepared pure by first washing with hydrochloric acid, and then recrystallising from the acid. The resulting salt was dried over solid caustic soda.

I. 0·272 gram of salt gave 0·0735 gram Pt = 27·02 per cent. Pt.
II. 0·618 gram of salt gave 0·162 gram Pt = 26·21 per cent. Pt.

Calculated for $(C_6H_5NCl_2,HCl)_2PtCl_4$ = 26·57 per cent. Pt.

α-Picoline,



$$\begin{matrix}CH_3\cdot CH\cdot N:CH\\ \|\qquad\qquad |\\ CH\cdot CH:CH\end{matrix}.$$

The dichloride was passed together with a stream of hydrogen through a tube filled with zinc-dust and heated to a low redness. A considerable quantity of picoline was produced, which was collected by passing through hydrochloric acid solution. In order to obtain the free base, the acid solution was made alkaline with soda and distilled, the distillate extracted by shaking with ether, and the ethereal solution of picoline dried by allowing it to remain with solid potash. On fractional distillation, after the ether had passed over, the thermometer rose rapidly to 128°, and the whole of the remaining contents of the flask distilled between 128° and 129°. From 15 grams of dichloropicoline, 2—3 grams of α-picoline were obtained. It was at once converted into a platinum salt and after several recrystallisations was obtained in large, yellow plates which did not contain any water of crystallisation, and were found to melt at 216—217° (221—222° corr.).

I. 0·3216 gram of salt gave 0·2862 gram CO_2 and 0·0907 gram H_2O.
II. 0·3495 gram of salt gave 0·1140 gram Pt.

	Calculated for $(C_6H_7N,HCl)_2PtCl_4$.	Found.	
		I.	II.
C	24·19	24·27	,,
H	2·69	3·13	,,
Pt........	32·55	,,	32·61

From the analysis, the substance evidently was a methylpyridine, but the melting point of the salt did not agree with that given by Ladenburg and Lange (*Annalen*, **247**, 6) as the melting point of the chloroplatinate of α-picoline, namely, 178°; moreover, the salt is supposed to contain 1 mol. H_2O. More recently, however, Stoehr

(*J. pr. Chem.* [2], **42**, 420—428) has given 195° as the melting point, and states that when pure the salt crystallises in the anhydrous condition in monoclinic tables. We therefore thought it necessary to prepare α-picoline by the best known methods, and compare the chloroplatinates thus formed.

The first method employed was heating methiodide of pyridine:—

$$C_5H_5N,CH_3I = C_6H_7NHI.$$

α-Picoline obtained in this way distilled almost completely between 127° and 129°, and, when converted into the chloroplatinate and purified by recrystallisation, gave a salt identical with ours in appearance and melting point. Moreover, the aurichloride was prepared from both picolines, and was found to melt at 183—184° (186—187° corr.), and the picrates were also identical, with a melting point of 169—171° (172—173° corr.). The second method employed was repeated recrystallisation of the platinichloride of a specimen of bone-oil picoline, whose boiling point lay between 128° and 129°; after more than 20 recrystallisations, the platinum salt melted at 210—211° (215—216° corr.), but we were unable to raise the melting point further. This, however, proved that the melting points given by Stoehr, and by Ladenburg and Lange, were probably too low. The α-picoline was also oxidised with permanganate of potash, and the picolinic acid m. p. 135—137° was obtained.

LXIV.—*Action of Light on Silver Chloride.*

By H. Brereton Baker, M.A., Dulwich College.

The fact that chlorine is evolved when silver chloride is darkened by exposure to light was first noticed by Scheele; it was supposed that a simple decomposition took place, and that the darkening was the consequence of the liberation of metallic silver. Shortly afterwards it was found, however, that darkening took place in presence of strong nitric acid and other solvents of silver, so that it was evident the metal could not have been set free.

Fisher, in 1814, supposed that the liberation of chlorine was due to the partial, instead of the total, decomposition of the silver chloride, and that a subchloride was produced. According to Vogel (*Ann. Phys. Chem.*, **119**, 497), the dark product is identical with the black powder obtained by Wöhler by the action of hydrochloric acid on silver suboxide. The observations of v. Bibra (*J. pr. Chem.*, **122**, 39), that the loss in weight of the silver chloride, in spite of the evolution of chlorine, was almost inappreciable, led me to investigate the question whether combination did not take place as well as decomposition, and whether the loss in weight caused by the undoubted escape of chlorine was not compensated for by the absorption of some other substance.

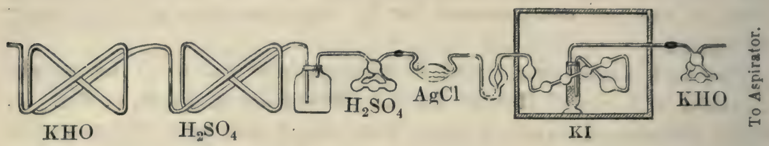
The first experiment tried I subsequently found to be nearly identical with one of Robert Hunt's (*Researches on Light*, p. 80). A small quantity of silver chloride was placed in a bulb blown on the end of a long tube, the open end of which dipped into potash solution. After a few days exposure, the liquid had risen several inches in the tube, although the temperature of the bulb was 1° higher and the barometric pressure was the same. After neutralisation with nitric acid, the solution gave a precipitate with silver nitrate; this seemed to show that oxygen was absorbed and chlorine liberated.

The next experiment was a modification of the first, there being two bulbs side by side, one of which contained the silver chloride, and the second, strong potash solution, to facilitate the absorption of the chlorine, the apparatus being filled with purified oxygen. In this case, after three days exposure to sunlight with constant shaking, the potash had risen 10 inches in the long tube, the conditions of temperature and pressure being nearly the same; on repeating the experiment, similar results were obtained. This shows that oxygen is absorbed during the darkening of the silver chloride, and as nothing dissolved on testing the blackened chloride with nitric acid, it was evident that no oxide of silver had been produced. It seemed possible that an oxychloride might have been formed, and this view was borne out by the stability of the darkened compound. On boiling with strong hydrochloric acid, the darkened substance becomes white, as we should expect it would if it contains an oxychloride.

An attempt was now made to determine the formula of the black substance. Until the appearance of Meldola's *Chemistry of Photography*, in 1889, I was ignorant that some work had been done in this direction by Professor Hodgkinson, whose results, however, beyond the brief mention in this book, have not been published.

To prepare the silver chloride used in the earlier experiments, standard silver was dissolved in nitric acid, and the solution diluted and filtered. Pure dilute hydrochloric acid was then added in excess, and the mixture boiled for some time. In order to prevent any admixture with organic matter, the washing of the chloride was performed by decantation only, and was continued until the washings gave no opalescence with silver nitrate.

After drying the silver chloride in an air-bath at 150°, it was powdered and allowed to cool in a desiccator over strong sulphuric acid. A weighed quantity of the chloride was then introduced into a weighed and dried bulb provided with two openings, and a current of air was drawn over the silver chloride by means of an aspirator.



During the experiment, the air was purified before entering the bulb by passing it through three inclined tubes containing strong potash solution, and it was then dried by passing it through similar tubes containing strong sulphuric acid. After leaving the chloride of silver bulb, the air, carrying with it the liberated chlorine, passed through a glass valve to prevent regurgitation, and thence into a set of bulbs containing a solution of potassium iodide; these bulbs were connected with a tube also containing potassium iodide, which showed by its remaining colourless that the absorption in the preceding bulbs was complete. The bulbs containing potassium iodide were shielded from the light by enclosure in a box. In order to prevent loss of chlorine, the tube at each joint was made to fit into the tube connected with it, and the intervening space was filled with paraffin, the whole joint being covered with india-rubber tubing. A set of bulbs containing caustic potash solution was placed between the potassium iodide bulbs and the aspirator to guard the former from any fumes from the laboratory. The whole apparatus was placed on a shelf across a south window. During exposure, the silver chloride bulb was continually shaken to submit fresh portions to the action of the light. This shaking had to be very cautiously done to prevent the disturbance of the joints. The amount of iodine liberated was estimated by sodium thiosulphate, and the amount of chlorine evolved was calculated from it; this weight was never greater than 15 milligrams.

The bulb containing the darkened chloride was weighed after the experiments, but it was found to be very difficult to obtain from the alteration in weight any trustworthy information as to the amount it had lost, silver chloride in its purest state being slightly hygroscopic; and on this account, the slight differences in weight, amounting to, at most, a milligram, were not considered sufficient evidence of the amount of change that had taken place.

The amount of oxygen was determined directly. A bottle with two tubulures was filled with purified chlorine; this was prepared, and the subsequent determination was made, in a room lighted by one gas jet only, so as to prevent any liberation of oxygen from the water by the chlorine. The chlorine was tested before and after the experiment, and found to be wholly absorbed by potash.

The bulb containing a weighed quantity of the darkened chloride was exhausted and gently heated while connected with the pump, to get rid of any air. The india-rubber connections, previously soaked in paraffin, were then closed by screw-clips and connected, the one with the bottle containing chlorine, and the other with a conducting tube previously filled with water and dipping under strong potash solution. The gas was collected in the laboratory tube of a gas-analysis apparatus. The bulb was then filled with chlorine, gently heated, and the gas slowly passed into the laboratory tube. The oxygen collected was drawn into the eudiometer of the apparatus and measured. It was always tested, either by explosion with hydrogen, or absorption with potassium pyrogallate, and if, as was occasionally the case, small quantities of nitrogen were found, corrections were made for the corresponding quantities of air.

The amount of silver in the darkened compound was determined by dissolving a weighed quantity of the darkened mixture in strong ammonia, collecting the precipitated silver on a filter, and weighing as metal.

In one experiment:—

The silver weighed 0·10633 gram.

The chlorine originally combined with this was 0·03482 gram.

Chlorine evolved = 0·01563 gram.

Chlorine in the darkened compound = 0·01919 gram.

The oxygen in the darkened compound = 0·00918 gram.

The percentages are:—

		Calculated for Ag_2ClO.
Ag......	78·94	80·75
Cl	14·25	13·27
O.......	6·81	5·98

The results of the experiments were not concordant, however, and a different method was tried.

A large bulb, fitted with a stoppered tubulure, was sealed on to the end of a long tube of 2 mm. bore, graduated in millimetres. The lower end of this was sealed into a U-tube, the other end of which could be closed by a stopper; the silver chloride was placed in the bulb. In the U-tube was placed a solution of potassium iodide to absorb the chlorine. The stopper of the bulb was covered with mercury during the exposure. The graduated tube was carefully calibrated by introducing a thread of mercury into it and measuring the length of it by means of a microscope. By weighing several such threads of mercury, it was found that the volume of a length of 1 cm. was 0·065 c.c. The volume of the bulb was determined by finding the weight of pure mercury required to fill it.

Before exposure, the apparatus was placed in a cellar in which the temperature is nearly constant, and left there for several hours. A thermometer, graduated to 0·1°, was hung by the bulb, and when both had acquired a constant temperature, readings were taken by means of a telescope.

During the exposure, the potassium iodide was protected from the light. The exposure needed was shorter than in the last experiments, since it was easier to shake the bulb, and so to expose fresh portions of the silver chloride to the action of the light.

The silver and the chlorine were determined as in the previous experiments. The results of this experiment lead to the formula $Ag_{13}Cl_{10}O_{16}$.

The probable defect in this experiment was that the temperature of the air inside the bulb was not obtained with sufficient accuracy. The method was therefore abandoned, and a third apparatus constructed. It consisted of a flask of about 130 c.c. capacity, in the neck of which was sealed a side tube, covered by the hollow stopper. In the stopper a small hole was drilled to correspond with the opening of the side tube. By this means communication could be made with the side tube by turning the stopper. The weighed silver chloride was placed in the flask. Into the stopper, one end of a roll of clean copper gauze was fixed, which served to absorb the chlorine. The flask, filled with oxygen, dried by sulphuric acid, was immersed in water for several hours to obtain a constant temperature. At the end of this time the stopper was opened for a moment by means of a long pair of tongs, so as to equalise the pressure between the contents of the flask and the atmosphere; the temperature of the water and the height of the barometer being read as accurately as possible. A mercury cap was then placed over the stopper, and the side tube filled with mercury to prevent any possibility of leakage.

When the exposure, which lasted generally about a month, with shaking at frequent intervals, was over, the mercury was removed from the stopper and the side tube, and the flask fixed in a trough of water which had been standing in a cellar of constant temperature. A weighed bulb, with a tap at one end and a thin tube at the other, was attached to the side tube of the flask with the tap open. The tap was closed with a pair of tongs, and the whole immersed in the water of the trough for a couple of hours. The tap was then opened, and on turning the stopper of the flask, water rushed into the bulb, which, after closing the tap, was cleaned and weighed. The necessary correction for the density of water at the temperature of the experiment having been made, an accurate measure of the difference in volume of the flask before and after the exposure was obtained. It would seem to be much more trustworthy than the measurement of small volumes of gases, since the error in weighing would necessarily be very small. In order to determine the weight of chlorine evolved, the stopper with the attached roll of copper was removed from the flask, and weighed in a tube whose ground neck just fitted the stopper. This was found to be necessary, because the oxychloride of copper formed was hygroscopic. The copper was then dissolved in dilute nitric acid and the solution precipitated by silver nitrate. The silver chloride was weighed, and from its weight the weight of the chlorine evolved could be found. The silver set free by ammonia was determined as in previous experiments. The results of one experiment of this series were:—

Weight of silver chloride taken, 51·3616 grams. The flask was filled with air, dried by sulphuric acid, at 10·6° and 768 mm.
The volume of water which entered the bulbs, corrected for temperature, was 3·7132 c.c.
Volume of the flask, 131·70 c.c.
Volume of air in the flask = 131·70 − volume of copper − volume of AgCl = 131·70 − 0·79 − 9·19 c.c. = 121·72 c.c. at 10·6° and 768 mm.
Volume of air at 0° and 760 = 118·4 c.c.
Volume of air after exposure = 121·72 − 3·71 c.c. = 118·01 c.c. at 10·6° and 754 mm.
Volume of oxygen absorbed = 5·7 c.c. at 0° and 760 mm.; this weighs 0·00817 gram.
Increase in weight of the copper = 0·0179 gram.
Chlorine in this determined as AgCl = 0·0139 gram.
Oxygen combined with copper = 0·0040 gram.
Oxygen absorbed by the silver chloride = 0·00417 gram.
Weight of silver set free by the action of ammonia = 0·0786 gram.
The chlorine originally combined with this = 0·0258 gram.
Chlorine left in darkened compound = 0·0119 gram.

Silver.......	$\frac{0\cdot0786}{107\cdot97}$	$Ag_{6\cdot3}$	Ag_{19}.
Chlorine	$\frac{0\cdot0119}{35\cdot35}$	$Cl_{3\cdot3}$	Cl_{10}.
Oxygen.....	$\frac{0\cdot0041}{15\cdot96}$	$O_{2\cdot6}$	$O_{7\cdot8}$.

In many of these experiments, the ratio only of chlorine evolved to oxygen absorbed was determined.

	Atoms of	
	Oxygen absorbed.	Chlorine evolved.
I.	1	0·70
II.	1	1·26
III.	1	1·12
IV.	1	1·26

I ascribe the discrepancy between these various results to the difficulty of working with such very small quantities of the darkened substance. In the experiment given above, out of 51 grams of silver chloride taken, the weight of the oxychloride produced was 0·09 gram. I believe, however, that there is another cause which affects the results. If darkened silver chloride be allowed to stand in the dark for some time, it will be noticed that it very slowly loses its colour, and becomes white. In order to find what caused this effect, an experiment was arranged with the apparatus used in Series B. The chloride was darkened as much as possible, and the absorption of oxygen was observed. Reduced to normal temperature and pressure, this was found to be 2·5 c.c. It was then allowed to stand in a dark room for two months, at the end of which time it had become nearly white, and a further absorption of oxygen was noticed of 0·26 c.c. It is impossible that the silver chloride could have been re-formed, since some of its chlorine had escaped. It seems likely that a higher oxychloride than the black one may be formed when the latter is kept in contact with oxygen. In connection with this point, it may be mentioned that it has been observed by Hunt and others that when black silver chloride is exposed to red light, it is bleached, a result which has been confirmed by Captain Abney, in working with collodion plates. It is possible that red light favours the production of this white substance. I am making experiments at the present time with the view of examining this change.

While the experiments described above were in progress, a paper was published by Dr. Richardson (this Journal, 1891, **59**, 536), in which the compound produced by the action of light on silver chloride was stated not to be an oxychloride, because no water had been obtained when the darkened chloride was heated in hydrogen. I repeated these experiments with the greatest care, and in each case found that water was produced. In three experiments, the oxygen in the darkened silver chloride had been determined by one of the other methods, and these determinations agreed with those made by Richardson's method within 2 per cent. It is possible that the difference in our results is caused by Richardson having used sulphuric acid to dry the hydrogen.

It was thought desirable to make some qualitative experiments, with the view of confirming the existence of combined oxygen in the darkened compound. Captain Abney has already shown that dry silver chloride does not darken in a vacuum, unless, he says, mercury or some other absorbent of chlorine, is present. In repeating his experiment, and performing those which follow, I used very carefully purified silver chloride. The ammoniacal solutions of the chloride, obtained in the quantitative determinations of silver, were treated in dim gas light, with very dilute nitric acid. The precipitated silver chloride was boiled repeatedly with distilled water, transferred to a beaker, previously heated nearly to redness to destroy any dust particles, and heated in an air-bath for several hours. It was then ground in an agate mortar, and with a spatula transferred to a tube, previously heated to redness, containing phosphorus pentoxide at one end and a drop of mercury in a bulb in the middle. It was then exhausted as completely as possible. After drying for three days, it was exposed to sunlight, and the silver chloride remained perfectly white for the six months during which the exposure was made.

A similar tube was made containing the silver chloride in pure carbon dioxide. The gas had been dried only by sulphuric acid. A slight change in colour occurred when exposed to light, and this was reversed in darkness. The small quantity of water present was probably decomposed, the action being reversible.

It was then thought advisable to see if silver chloride was darkened in dried oxygen. A tube was filled with oxygen, having phosphorus pentoxide at one end, and pure silver chloride at the other. This was exposed to bright sunlight, and not the slightest change in colour could be detected.

In the early stages of the research, some experiments were undertaken by some of my students and myself, with the object of ascertaining if silver chloride darkened in liquids which contained no oxygen. Sealed up in purified dried benzene, with only the vapour above the liquid, it darkened rapidly. The dark substance was black, with no tinge of blue. It seemed possible that it was not the ordinary product of the action. On testing, it was found to be metallic silver, being entirely soluble in dilute nitric acid. This was no doubt a simple case of reduction of the chloride to metal. Carbon tetrachloride was next selected, as a liquid which does not contain oxygen, neither is it capable of acting as a reducing agent. A specimen was purified by fractional distillation, and allowed to stand over phosphorus pentoxide for a week. It was then introduced into a tube containing dried silver chloride. The liquid was then boiled, and the tube sealed. On exposure to light, the chloride darkened immediately. On testing the darkened product, it was found to be metallic silver, produced by the presence of unsuspected traces of alcohol in the tetrachloride. I then attempted to prepare pure carbon tetrachloride by the action of chlorine on carbon bisulphide. After washing with water, the product was distilled from metallic mercury, to free it from chlorine. Silver chloride darkened slowly under this also. The residue was soluble in nitric acid, and the solution gave a white precipitate with barium nitrate, showing that silver sulphide had been produced. Some carbon tetrachloride was obtained from Kahlbaum, of Berlin, and was found to contain no free chlorine. It was dried by allowing it to stand over phosphorus pentoxide for a week. On sealing up this with silver chloride, air being excluded, it gave not the slightest darkening in bright sunlight. It was allowed to stand for three months in a south window, and no change in colour was ever observed. One such tube, after remaining unaltered for a month, began one morning to show a change in colour. The top layer of the silver chloride became covered with a violet film. On careful examination, a minute crack was observed at the point where the tube had been sealed. The tube was opened. No inrush of air took place, showing that the space above the liquid was already full of air. On leaving the tube for an hour in sunlight, the silver chloride darkened as completely as if it had been freely exposed to air. Several tubes have been made with the same result, thus establishing the fact that under pure carbon tetrachloride, silver chloride does not darken.

A very convincing proof of the existence of an oxychloride was obtained in an unexpected manner. An attempt was made to separate the darkened compound by dissolving away the unaltered chloride in a strong solution of potassium chloride. It was found that all the substance was dissolved, and, on dilution with water, pure silver chloride was precipitated. If the dark substance was really an oxychloride, some action must have taken place which would liberate alkali. Some of the solution was diluted with a large quantity of water, filtered from the precipitated silver chloride, and tested with a solution of phenolpthaleïn. A distinct pink colour was observed. In a similar experiment, using the utmost precautions to avoid error, neutral litmus solution was turned distinctly blue.

General Conclusions.

The dark substance produced by the action of light on silver chloride is an oxychloride.

The formula of the oxychloride is probably Ag_2ClO.

When the darkened substance is kept in the dark, a fresh absorption of oxygen takes place, probably due to the formation of a white oxychloride.

LXV.—*Fermentation of Arabinose with the* Bacillus ethaceticus.

By Percy F. Frankland, Ph.D., B.Sc., F.R.S., and John MacGregor, M.A. (Edin.), Forster Scholar in University College, Dundee.

It has been previously shown by one of us that pure growths of this organism cause the fermentation of a number of carbohydrates, of mannitol and glycerol, as well as of calcium glycerate, and a detailed description of the products obtained from the three last-mentioned bodies, as well as from dextrose, has been given (*Proc. Roy. Soc.*, **46**, 345; *J. Chem. Soc.*, Trans., 1891, **59**, 81 and 96; 1892, **61**, 432). In each case the products obtained consisted chiefly of ethyl alcohol and acetic acid, together with traces of succinic acid and variable proportions of formic acid.

The substances thus fermented by this organism all possess either a three- or six-carbon molecule, indeed we have hitherto failed to ferment either glycol or erythrol, and hence it was of particular interest to ascertain the nature of the fermentation products resulting from the decomposition of the five-carbon molecule of arabinose.

The specimen of arabinose which we have used in this investigation was obtained from Dr. Schuchardt, and we have determined its purity by means of the following tests:—

The specific rotation of a 10 per cent. solution, after standing 24 hours, was $[\alpha]_D = 104°$. The melting point was found to be 152—153°. Scheibler (*Ber.*, **1**, 108) gives the melting point as 160°. Our specimen was accordingly recrystallised from alcohol to see if this discrepancy was caused by any impurity. The crystals thus obtained were small, colourless prisms radiating from centres. The melting point was still 152—153°. A 4 per cent. solution of this recrystallised arabinose gave at first $[\alpha]_D = 118{\cdot}3°$, but after standing until the rotation was constant $[\alpha]_D = 106°$; temperature 18°. Parkus and Tollens (*Ber.*, **23**, Ref. 401) have obtained a much greater range for $[\alpha]_D$, namely, from 156·6° to 104·5°. Bauer (*Ber.*, **22**, 835) gives the range of $[\alpha]_D$ from 116·7° to 104·4°.

The phenylhydrazine compound prepared with our specimen melted at 156—157°; Kiliani (*Ber.*, **20**, 339) gives 158°.

Günther and Tollens (*Ber.*, **23**, 1751) have described a method for the quantitative estimation of arabinose by distillation with hydrochloric acid and titration of the furfural so obtained with phenylhydrazine. The yield of furfural is said to be about 50 per cent. of the weight of the arabinose. Our specimen, when examined by this method, gave 49·83 per cent. of its weight of furfural; thus, 0·1967 gram arabinose yielded 0·09801 gram furfural = 49·83 per cent.

First Series of Fermentations.

In the first instance, the arabinose was fermented in flasks plugged with cotton wool, thus admitting of the free diffusion of air into them. The fermentation was carried out in duplicate, each of the flasks being charged with the following materials :—

Arabinose	10 grams	diluted to 1000 c.c. with distilled water.
Peptone	1 ,,	
Carbonate of lime.	10 ,,	
Salt solution	100 c.c.	

It is needless to say that all the necessary precautions of sterilisation, &c., as described in previous communications, were observed. Each flask was inoculated with a pure growth of the *B. ethaceticus*, taken from a fermenting solution of mannitol, and was then placed in an incubator maintained at 38°. The liquids were in a state of fermentation on the fourth day, and continued visibly disengaging gas over a period of one month.

At the conclusion of the fermentation, the contents of the two flasks were submitted to chemical examination in the manner described in former communications.

The alcoholic liquid obtained by distilling the fermented contents of the flask was oxidised with potassium dichromate and sulphuric acid, and the volatile acids thus produced were converted into barium salts, of which there were obtained from

Flask No. 1. 3·423 grams of barium salt, yielding 91·10 per cent. $BaSO_4$, corresponding to 1·235 gram ethyl alcohol.

Flask No. 2. 3·130 grams of barium salt, yielding 91·06 per cent. $BaSO_4$, corresponding to 1·129 gram ethyl alcohol.

From the above determinations, it will be seen that the percentage of $BaSO_4$ yielded by these barium salts was slightly, but distinctly, lower than that yielded by pure barium acetate, which gives 91·37 per cent. $BaSO_4$. This points to the presence of a very small quantity of some alcohol higher than ethylic, which is also substantiated by the subsequent fermentations.

Volatile Acids.—After distilling off the alcohols as above, the volatile acids were liberated by the addition of the calculated quantity of hydrochloric acid, and the distillates collected in three distinct fractions, each of which was separately converted into barium salts, thus:—

Flask, *No.* 1.	*Flask*, *No.* 2.
Fraction I gave 3·0965 grams barium salt, yielding—	Fraction I gave 2·8370 grams barium salt, yielding—
(1) 90·76 per cent. $BaSO_4$.	(1) 90·63 per cent. $BaSO_4$.
(2) 90·72 „ „	(2) 90·89 „ „
Fraction II gave 2·0665 grams barium salt, yielding—	Fraction II gave 2·5530 grams barium salt, yielding—
(1) 91·08 per cent. $BaSO_4$.	(1) 91·14 per cent. $BaSO_4$.
(2) 90·87 „ „	(2) 91·18 „ „
Fraction III gave 0·2895 gram barium salt, yielding—	Fraction III gave 0·492 gram barium salt, yielding—
90·72 per cent. $BaSO_4$.	90·57 per cent. $BaSO_4$.

In all cases the percentage of $BaSO_4$ is distinctly lower than that required by barium acetate (91·37 per cent. $BaSO_4$), pointing to the presence of an acid of higher molecular weight. The quantity of this acid must, however, be so slight, that, for practical purposes, it may be neglected, and the whole of these barium salts calculated as acetic acid, of which there are then in No. 1 2·566 grams, and in No. 2 2·768 grams.

The ratio between the alcohol and acetic acid in these fermentations is:—

No. 1.	No. 2.
$C_2H_6O : C_2H_4O_2$	$C_2H_6O : C_2H_4O_2$
$1 : 2{\cdot}08$	$1 : 2{\cdot}45$

and inasmuch as all the errors of experiment tend in the direction of finding too little alcohol, it is probable that the lower of the above proportions is the more accurate. This corresponds closely with that of 2 mols. of alcohol to 3 of acetic acid—

$$\begin{array}{ll} 2C_2H_6O : 3C_2H_4O_2 = 1{\cdot}96 \\ \;\;2\,(46) \quad\;\; 3\,(60) \end{array}$$

After removal of the volatile acids, there was, as usual in these fermentations, a small quantity of brown insoluble matter left, which, on drying at 100°, amounted to

No. 1.... 0·1935 gram. No. 2.... 0·1660 gram.

Subsequently, by extraction with ether, there was obtained

from No. 1...... Determination lost.
„ No. 2...... 0·089 gram of succinic acid.

From the residues, after extraction with ether, nothing but a small quantity of gummy matter soluble in alcohol could be obtained.

Fermentation of Arabinose in a Closed Space: Determination of Gaseous Products.

We now proceeded to investigate the fermentation when conducted under circumstances permitting of the collection of the gaseous products. The solutions of arabinose were placed in bottles, each provided with a delivery tube dipping into a mercury bath over which the gases were collected. The arrangement of the experiment was precisely similar to that already described by one of us (Trans., 1891, **59**, 260).

The fermentation was carried on in duplicate, thus:—

No. 1 bottle.			No. 2 bottle.
Arabinose......	8 grams	made up to 400 c.c. with distilled water.	Ditto.
Peptone	0·4 „		
$CaCO_3$.........	4·0 „		
Salts solution ..	40 c.c.		

The evolution of gas took place as follows:—

No. 1.		No. 2.	
Days after inoculation.	Total volume of gas collected (corr. to 0° C. and 760 mm.).	Days after inoculation.	Total volume of gas collected (corr. to 0° C. and 760 mm.).
5	7·3	5	6.9
6	9·0	6	8·8
9	197·9	9	179·8
10	320·9	10	270·8
11	419·3	13	351·3
13	497·0	16	441·4
15	567·6	20	496·7
20	681·7	38	561·2
38	787·5	66	583·9
66	809·5		

The evolution of gas is most conveniently studied by reference to the diagram (next page), in which the ordinates represent the volumes of gas in c.c. and the abscissæ the days after inoculation of the arabinose solutions.

Samples of the gas evolved were from time to time submitted to analysis, with the following results:—

Gases evolved from Fermentation of Arabinose.

No. 1.

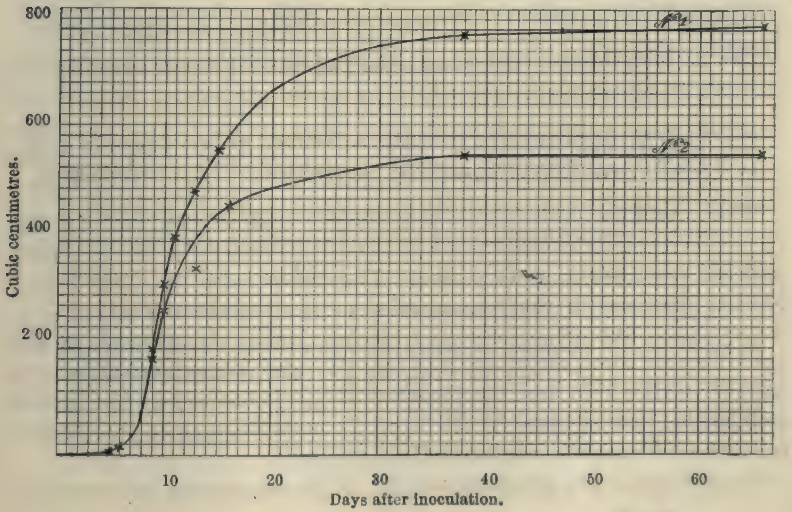
	I. 8th day.	II. 9th—10th day.	III. 10th—12th day.	IV. 19th—37th day.	Mean of analyses II, III, and IV.
CO_2	27·86	63·96	64·83	61·30	63·36
O..	5·78	0·17	0·09	0·14	0·13
H..	26·67	35·53	34·89	38·10	36·17
N..	39·69	0·34	0·19	0·46	0·34
	100·00	100·00	100·00	100·00	100·00

No. 2.

	I. 5th—8th day.	II. 9th—12th day.	III. 19th—37th day.	Mean of analyses II and III.
CO_2...	33·80	56·36	56·76	56·56
O.....	1·54	0·16	0·33	0·25
H.....	37·77	43·37	41·99	42·68
N.....	26·89	0·11	0·92	0·51
	100·00	100·0	100·00	100·00

FERMENTATION OF ARABINOSE.

Upper curve, Arabinose No. 1.
Lower ,, ,, No. 2.



Thus, not only was there a very considerable difference in the volumes of gas given off in the two fermentations, but in composition also there was a marked difference, the gas in No. 1 being richer in carbonic anhydride and poorer in hydrogen than that from No. 2. This difference finds its explanation in the nature of the other products, and will be referred to again.

From the above volumes and composition it can be calculated that there were obtained from

No. 1	292·8 c.c.	of hydrogen	0·0262 gram.
	516·7 ,,	carbonic anhydride	1·0185 ,,
No. 2	249·2 c.c.	of hydrogen	0·0223 gram.
	334·7 ,,	carbonic anhydride	0·6598 ,,

Treating the fermented liquids in the same manner as previously described (see p. 738), there were obtained by oxidation of the alcoholic portion from

No. 1. 1·486 gram of barium salt, yielding 90·38 per cent. $BaSO_4$, and corresponding to 0·5361 gram of ethyl alcohol.

No. 2. 1·248 gram of barium salt, yielding 90·47 per cent. $BaSO_4$, and corresponding to 0·450 gram of ethyl alcohol.

Of volatile acids, there were obtained from

No. 1. 1·5645 gram of barium salt, yielding 92·68 per cent. $BaSO_4$, and corresponding to

0·1818 gram of barium formate = 0·0737 gram of formic acid.
1·3827 ,, ,, acetate = 0·6507 ,, acetic acid.

No. 2. 1·4025 gram of barium salt, yielding 93·32 per cent. $BaSO_4$, and corresponding to

0·2426 gram of barium formate = 0·0983 gram of formic acid.
1·1599 ,, ,, acetate = 0·5458 ,, acetic acid.

These results again show that formic acid is produced in the closed fermentations, even when it is entirely absent in the open ones induced by the same organism. They show also that the ethyl alcohol produced in the fermentation of the arabinose is mixed with a very small quantity of a higher alcohol, just as was the case in the open fermentation, and doubtless there is also a small quantity of a higher volatile acid, but the presence of this is masked by the formic acid, whilst its presence in the open fermentations was manifested, owing to its being only mixed with acetic acid.

In addition to the products referred to above, as well as a trace of succinic acid, there is, also, another unidentified acid formed. We have obtained evidence of its presence by determining the total quantity of carbonate of lime dissolved in the fermentation, and find this to be in

	Gram.		Gram.
No. 1	1·025	No. 2	0·943
Corresponding to CO_2.	0·4510	Corresponding to CO_2.	0·4149

These quantities of calcium carbonate have been dissolved, of course, by the acids formed, of which we have determined the amount of the formic and acetic as above. Now the carbonic anhydride corresponding to the formic and acetic acids found amounts to

No. 1.... 0·2739 gram CO_2 No. 2.... 0·2471 gram CO_2,

thus leaving carbonic anhydride due to the decomposition of calcium carbonate by the unknown acid in

No. 1.... 0·1771 gram CO_2 No. 2.... 0·1678 gram CO_2.

On subtracting the whole of the carbonic anhydride, due to decomposition of the calcium carbonate, from the total carbonic anhydride found by gas analysis, there is a balance of

No. 1.... 0·5675 gram CO_2 No. 2.... 0·2449 gram CO_2,

and this is the only discrepant result obtained in the two fermentations. This residual CO_2 in No. 1 is almost the exact amount required to yield formic acid with the hydrogen found (0·0263 × 22 = 0·5786 gram), whilst the residual CO_2 in No. 2 is much too little for this purpose, for 0·0223 × 22 = 0·4906 instead of 0·2437 gram. It would appear probable, therefore, that this deficiency of CO_2 must have remained dissolved as bicarbonate in the fermented liquid, and thus escaped measurement, for it will be seen on reference to the gas analyses (p. 741) that the gas evolved in Fermentation No. 2 had a strikingly lower percentage of CO_2 than that from No. 1.

Assuming, therefore, that we are justified in calculating the hydrogen with this residual carbonic anhydride into formic acid, we may tabulate the products of these fermentations thus:—

	No. 1. Gram.	No. 2. Gram.
Ethyl alcohol found..............	0·5361	0·450
Acetic acid found................	0·6507	0·5458
Formic acid found	0·0737	0·0983
Total CO_2 found by gas analysis ..	1·0185	0·6598
Total CO_2 from decomposition of $CaCO_3$ by acids formed.........	0·4510	0·4149

	No. 1. Gram.	No. 2. Gram.
CO_2 due to decomposition of $CaCO_3$ by acetic and formic acids	0·2739	0·2471
CO_2 due to decomposition of $CaCO_3$ by unidentified acid	0·1771	0·1678
Residual CO_2 due to fermentation	0·5675	0·2449
Hydrogen found by gas analysis	0·0263	0·0223
Total formic acid by calculation	0·6786	0·6112

With the exception of the residual carbonic anhydride in No. 2, all these products are present in almost identical proportions in the two fermentations; thus, the relationship between them is well exhibited by comparing their amounts with the quantity of hydrogen found, taken as unity—

	H :	C_2H_6O :	$C_2H_4O_2$:	CH_2O_2 :	CO_2 equivalent of unidentified acid.
No. 1	1 :	20·4 :	24·7 :	25·8 :	6·7
No. 2	1 :	20·2 :	24·5 :	27·4 :	7·5

On dividing these relative weights by the molecular weights, we obtain the following molecular relationships:—

	No. 1.	No. 2.
C_2H_6O	0·44	0·44
$C_2H_4O_2$	0·41	0·41
CH_2O_2	0·56	0·60
CO_2 equivalent of unidentified acid	0·15	0·17

which figures again closely approximate to the following integral molecular values:—

$$\left.\begin{array}{l}\text{One molecule } CO_2 \text{ equiva-}\\ \text{lent to unidentified acid..}\end{array}\right\} + 3C_2H_6O + 3C_2H_4O_2 + 4CH_2O_2.$$

The quantity of material at our disposal was altogether insufficient to permit of our investigating the nature of the unidentified acid in question.

The principal conclusions at which we have arrived in this investigation are the following:—

1. Arabinose is fermentable with the *Bacillus ethaceticus.*

2. The products are essentially similar to those obtained in the fermentation of other carbohydrates and polyhydric alcohols by this organism, and consist of ethyl alcohol, acetic acid, carbonic anhydride, and hydrogen, together with a trace of succinic acid, whilst, if

the fermentation is carried on in a closed space, a considerable quantity of formic acid is also produced.

3. The carbonic anhydride and hydrogen are evolved in proportions closely corresponding to that in which they are present in formic acid, namely, equal volumes or molecules.

4. In addition to the above products, we have, as in fermentations of other carbohydrates with this bacillus, also obtained evidence of the presence amongst the products of another acid, the nature of which we have not yet been able to determine.

5. The products of the decomposition of the arabinose are approximately formed in the following molecular proportions:—$3C_2H_4O_2 : 3C_2H_6O : 4CH_2O_2 : CO_2$ equivalent of unidentified acid, in which the whole of the evolved carbonic anhydride and hydrogen is represented as formic acid.

6. In the fermentations conducted in flasks closed with cotton wool only, the alcohol and acetic acid were found in the proportion $2C_2H_6O : 3C_2H_4O_2$.

Thus, in the fermentation of arabinose by this micro-organism, the proportion of acetic acid to alcohol is greater than in that of dextrose, and still greater than in that of mannitol and glycerol, but less than in that of glyceric acid.

LXVI.—*The Atomic Weight of Palladium.*

By G. H. Bailey, D.Sc., Ph.D., and Thornton Lamb, 1851 Exhibition Scholar, Owens College.

The atomic weight of palladium was first determined by Berzelius (*Ann. Chim. Phys.*, **8**, 177) in the year 1813 by a synthesis of the sulphide and by the reduction of the chloride by means of mercury. The values obtained from these experiments were 711 and 704 respectively (oxygen = 100). Fifteen years later (*ibid.*, **13**, 454), having recognised that these numbers could not be regarded as very accurate, he repeated the determination, using potassium palladious chloride. He found this difficult to prepare in the anhydrous condition without running the risk of decomposing the salt, but, notwithstanding this, he estimated after reduction in hydrogen—

a. The amount of palladium in a given quantity of the salt.

b. The amount of potassium chloride washed out from the residual palladium.

c. The chlorine given off when the salt is strongly heated.

His numbers, as deduced from these experiments and recalculated by Clarke (*Constants of Nature*, v, 257), are:—

From percentage of	metal	106·612
,,	KCl	104·674
,,	chlorine	110·796

Berzelius himself accepted the first of these values as representing the atomic weight of palladium.

In 1847, Quintus Icilius published a dissertation in which he refers to some experiments done by himself, which led him to take 111·879 as the atomic weight of palladium.

At the time we commenced our investigation, these were the only estimations which had been made, though, while our work was in progress, a paper was published by Keiser (*Amer. Chem. Journ.*, **11**, 398), from which it appeared that he had used in his determinations palladammonium chloride, $Pd(NH_3Cl)_2$, a salt which our preliminary investigation had already led us to adopt as apparently well adapted for the purpose. It does not, however, appear from Keiser's paper that any special precautions were taken to ensure the purity of the palladium used; moreover, the details given with regard to the preparation of the salt and its analysis are too meagre to enable us to draw conclusions as to the cause of the difference between his results and those we have obtained.

The value assigned as the result of these experiments, namely, 106·35, is almost identical with that of Berzelius already quoted.

In view of the importance of a redetermination of the atomic weights of the platinum metals and of the interest which attaches to the work done during the last few years by Seubert and others, we decided to continue our investigation, especially as, from a communication kindly made to us by Professor Seubert, it appeared that he had no immediate intention of entering upon a redetermination of this atomic weight.

Preparation of Palladium.

The raw material for the preparation was obtained from the Sheffield Smelting Company, and consisted of residues rich in palladium which had been accumulated by them for some time. It was found to contain about 95 per cent. of palladium associated with small quantities of other platinum metals, chiefly platinum, and also copper and iron.

The material was first extracted with hydrochloric acid, and when nothing more passed into solution, the residue was separated by filtration, washed, and dissolved in *aqua regia*. The small quantity of insoluble matter was then removed, and the solution boiled down several times with hydrochloric acid until the nitric acid was entirely expelled. The palladious chloride thus obtained was precipitated by means of mercuric cyanide, the precipitate washed thoroughly (a very slow process, owing to its gelatinous character), and ignited. The metal left on ignition was redissolved in hydrochloric acid with the addition of some nitric acid as before, and then thrown down by means of potassium chloride prepared by Stas' method; the potassium palladious chloride thus obtained being reduced in hydrogen and washed till free from potassium chloride. This treatment was repeated several times.

The metal finally obtained was practically unacted upon by hydrochloric acid. It was again dissolved, the excess of acid expelled, and ammonia added until the precipitate at first thrown down was redissolved, a slight residue which remained being rejected. Gaseous hydrogen chloride was then passed into the clear solution after it had been sufficiently diluted to prevent the precipitation of ammonium chloride, and the yellow palladammonium chloride precipitate collected in several fractions. The earlier and later fractions were rejected, the palladium used in the investigation being obtained from the intermediate portions by reduction in hydrogen.

Examination of Salts of Palladium.

The salts investigated were those which seemed likely to be suitable for our purpose, namely:—

a. Palladious cyanide.
b. Palladammonium cyanide.
c. Potassium palladious chloride.
d. Palladammonium chloride.

Palladious Cyanide.—It was found that on heating a small quantity of this salt in the apparatus already described by one of us (*Chem. News*, **54**, 302), and gradually raising the temperature, no cyanogen was evolved, and the weight remained constant at 220°. An analysis showed, however, that a small quantity of water still remained attached to the salt, and when it was sought to get rid of this by heating to a still higher temperature, decomposition ensued, accompanied by the formation of paracyanogen. The cyanide is, therefore, not adapted for the determination of an atomic weight.

Palladammonium Cyanide.—This was prepared by passing pure hydrogen cyanide into an ammoniacal solution of palladious chloride and recrystallising the salt which separated out. It was obtained in splendid crystals, and appeared to be a most promising substance.

Some difficulty was experienced in obtaining it perfectly anhydrous, but this was overcome. Even below 100°, the salt begins to give off ammonia, and it was thought that a determination might be made (*a*) of the ammonia, (*b*) of the palladious cyanide then remaining, (*c*) of the palladium ultimately left by the ignition of the palladious cyanide. It was found, however, that there was no sharp line of demarcation in the decomposition, so that, in view of the advantages presented by the corresponding chlorine derivative, the latter seemed preferable, more especially as at that time we were under the impression that it would be possible to separately determine the chlorine and the palladium, if not also the ammonia in it. Some determinations which were made with this cyanide, however, rendered it probable that the atomic weight did not exceed 106.

Potassium Palladious Chloride.—The difficulty of obtaining this salt in an anhydrous condition, originally pointed out by Berzelius, constitutes a real objection to its use for an atomic weight determination. This objection, however, entirely disappears if, instead of taking the relation between the *salt* and its constituents as he did, we ascertain the ratio which the constituents potassium chloride and palladium bear to each other. This ratio is manifestly independent of the presence of moisture in the salt.

A quantity of the double salt was therefore prepared by precipitating a concentrated solution of palladious chloride by means of potassium chloride, avoiding the presence of oxidising agents. The crystals were carefully separated from the mother liquor, several times washed with small quantities of water, and dried at the ordinary temperature under reduced pressure.

The salt was then heated in a stream of pure, dry hydrogen at as low a temperature as possible until complete reduction had taken place.

TABLE I.

Denomination of sample.	KCl found.	Pd found.	Atomic weight of Pd, H = 1.
K I	1·49767	1·05627	104·945
K II	0·90484	0·63738	104·820

In consequence of the difficulty of preparing the pure salt in sufficiently large quantity, and the errors incidental to its analysis, we at the time saw no hope of achieving results at all comparable in point of accuracy with those attainable from palladammonium chloride. With a larger amount of pure material, such as we at present have, and the experience gained from the determinations made, we believe, however, that a good result may yet be arrived at by this method, and shall take some future opportunity of continuing the investigation along these lines. We have every reason to consider the values deduced from the experiments quoted to be too low.

Palladammonium Chloride.

This salt can be obtained in a very pure condition, as already described in the preparation of palladium, and when the earlier and later portions are rejected several fractions can be obtained which show no appreciable variation in character or composition. It separates out in exceedingly minute, pale-yellow crystals, and, after decanting the mother liquor, the product is washed repeatedly by aid of the filter-pump. It is practically insoluble in water or dilute acids and can be readily dried under diminished pressure at the ordinary temperature. It possesses the further advantage of not being hygroscopic, and on several occasions portions of a gram or more having been exposed to air increased in weight two or three tenths of a milligram during the first hour, and after that showed little or no further variation.

Determination of Chlorine.

Method of Analysis.—From 1·5 to 3 grams of the salt were weighed out in a porcelain boat and reduced by heating in a stream of hydrogen. The hydrogen was prepared from pure zinc and sulphuric acid, and passed successively through alkaline permanganate of potash, nitrate of silver, and potash, and then over a layer of glass wool. The combustion tube used was about 6 feet in length, two-thirds of it projecting outside the furnace, so that the greater part of the ammonium chloride formed in the decomposition might condense in this part. Ammonium chloride was prevented from depositing on the fore part of the tube by heating this first, and also by carefully regulating the supply of hydrogen. Notwithstanding all possible precautions, however, it was not found possible to condense the whole of the ammonium chloride in the tube.

The ammonium chloride washed out of the tube, and that which was carried over into the wash bottles succeeding it, was precipitated by the addition of silver nitrate, using all the precautions adopted by Stas. In some of the experiments the silver chloride was determined gravimetrically. The following table gives the results obtained:—

TABLE II.

Denomination of sample.	$Pd(NH_3Cl)_2$ taken.	AgCl found.	Atomic weight of Pd.	
			O = 1.	H = 1.
B II	1·24276	1·682249	6·6771	106·566
R II	1·08722	1·468448	6·7065	107·036
R V	1·47666	2·000164	6·6685	106·430
R VI......	1·34887	1·837957	6·5900	105·177
R VII.....	1·74569	2·362320	6·6812	106·368
	Mean.... =		6·6646	106·368

In the calculation of these values (the weighings having been corrected), the atomic weights used were—

Ag = 107·66
Cl = 35·37
N = 14·01
H = 1·00

The most cursory examination of these numbers shows that the variations are much greater than can be accounted for by the ordinary errors of experiment, nor are they attributable in any considerable degree to differences in the composition of the salt employed in the determinations. We found as a matter of fact that various causes were at work which interfered with the accuracy of the results.

In the first place, though we interposed several wash bottles, columns of moistened glass wool, or even collected and washed the hydrogen used in the reduction, small quantities of ammonium chloride were carried forward and lost, and this even when the hydrogen used for the reduction was passed very slowly. Secondly, there is little doubt that secondary decompositions occur during the process of reduction, and the combustion tubing used for the process was acted upon at the moderate temperatures employed to a greater extent than seemed likely to arise from the corrosive action of ammonium chloride. Amongst others, Seubert seems to have found the same difficulties in the determination of chlorine in such decompositions, and thought the differences might be due to the india-rubber cork which he used, taking up hydrochloric acid. A remarkable passage occurs in the paper already referred to, in which Berzelius describes his experiments on palladium salts; we quote it, not only because it bears directly on this question, but also since it is particularly suggestive in view of recent investigations. Speaking of the palladammonium chloride which he had prepared, he describes it as a substance "welcher bei trockner Destillation zuerst ein wenig freies Ammoniak, dann Salzsaüre, Stickgas und endlich Salmiak giebt, während reines metallisches Palladium zur Hälfte seines Gewichts zurückbleibt. Dieses Salz ist dem *Mercurius præcipitatus albus* der Pharmaceuten analog, und besteht aus einem Atom Palladium chlorür und einem Doppelatome Ammoniak.

"Die Entstehung desselben gründet sich darauf, dass das Chlor des Chlorürs mit dem Ammoniak bildet: Chlorammonium, Stickgas und Salzsaüre."

As they stand, the results in Table II point to a value higher than 106 as the atomic weight of palladium, and so far are in agreement with the number obtained by Berzelius, but, as we shall see later, the value obtained from the palladium contained in the salt in experiments carried out with extreme care falls about one unit lower.

We have tried the distillation of the salt with pure caustic soda, so as to determine the ammonia given off and the chlorine remaining in the residue, but the reaction is incomplete, and neither this nor any of the other methods which we have thus far attempted have enabled us to check the results obtained in the experiments quoted above. Although the numbers found are sufficiently near to indicate that the salt has the composition which has been assigned to it, there can be no doubt of the desirability of an indepeudent determination which shall afford more complete proof of its constancy of composition than is given in the succeeding experiments.

Determination of Palladium.

The tube in which the reduction had been performed was allowed to cool down to considerably below a red heat, and the hydrogen was then displaced by air. The boat now containing the palladium was withdrawn and introduced into a porcelain tube, which was first exhausted and then exposed to a red heat in a charcoal furnace. Any gases evolved were drawn off by means of a Sprengel pump, the heating being continued for about two hours, at the end of which time no more gas appeared.

In order to avoid the possibility of alteration in the boat itself, it was wrapped in platinum foil, and in no case was the boat found to undergo loss of weight. Indeed, a boat which had been used for a number of determinations was not found to vary more than $\frac{1}{10}$ milligram. The palladium sintered together, forming a coherent mass resembling silver in appearance, although a little more dull. More than 20 determinations were made in this way in five series, two of which were with imperfectly purified material. The results of the *whole* of the determinations in the last three series, except those made with the earlier and later fractions, are given in the succeeding tables. Series A and B were preparations from palladium obtained by a method different from that used in Series C.

Table III.

Series A.

Denomination of fraction.	Weight of $Pd(NH_3Cl)_2$.	Weight of Pd.	Percentage of Pd.	Atomic weight, H = 1.
D II	1·890597	0·947995	50·1426	105·353
D III......	1·874175	0·940271	50·1698	105·468

$Pd(NH_3Cl)_2$: Pd :: 3·764772 : 1·888266

Pd : O :: 6·60463 : 1·000000

Pd : H :: 105·410 : 1·000000

Series B.

Denomination of fraction.	Weight of $Pd(NH_3Cl)_2$.	Weight of Pd.	Percentage of Pd.	Atomic weight, H = 1.
E II	1·307076	0·654687	50·0878	105·123
E III	1·340045	0·673207	50·2376	105·754
E IV	1·905536	0·955950	50·1671	105·359
E V	1·685582	0·846472	50·2184	105·672

$Pd(NH_3Cl)_2$: Pd :: 6·238239 : 3·130316
Pd : O :: 6·6108 : 1·000000
Pd : H :: 105·508 : 1·000000

Series C.

Denomination of fraction.	Weight of $Pd(NH_3Cl)_2$.	Weight of Pd.	Percentage of Pd.	Atomic weight, H = 1.
F II	1·691028	0·849120	50·2132	105·651
F III	2·112530	1·059690	50·1621	105·435
F IV	2·110653	1·057910	50·1224	105·267
F V	1·969100	0·988155	50·1838	105·523

$Pd(NH_3Cl)_2$: Pd :: 7·883311 : 3·954875
Pd : O :: 6·60767 : 1·000000
Pd : H :: 105·458 : 1·000000

Taking the mean of the three series, we have :—

Series A......	105·410
„ B......	105·508
„ C......	105·458
Mean =	105·459

a value agreeing with Series C, on which we have reason to place the greatest reliance.

The Weighings.

The balance used was by Oertling, and had already been employed by one of us in the determination of the atomic weight of zirconium and also in other atomic weight determinations made at the Owens College.

The readings were made by means of a telescope, the image of the scale being reflected along the line of vision by mirrors.

The stability and sensibility of the instrument may be judged by the fact that in a series of weighings, extending over a fortnight, the extreme variation of the zero point did not exceed 0·3 of a division, whilst the displacement produced by the addition of a milligram was 11·1 divisions, and never varied more than 0·2 of a division.

We are of opinion that the readings may be relied upon to 0·25 of a division.

The weights used were an excellent set by Staudinger. They had several times been carefully compared, and in the calculations allowance was made for the slight inaccuracies which had been observed in them. The boat and palladium were enclosed in a stoppered bottle and every precaution was taken to avoid the absorption or condensation of moisture during the operation of weighing.

The weighings have also been reduced to *vacuo*. For this purpose, the specific gravities of the substances used were determined, and in the case of palladium in the state in which it occurred after reduction, the specific gravity was found to be 11·12, that of the palladammonium chloride being 2·55.

In conclusion, as the atomic weights of the metals of the platinum group have now been all redetermined, it is not inappropriate to place them together for the sake of comparison:—

Ruthenium.	Rhodium.	Palladium.	Silver.
101·4	102·7	105·5	107·7
Osmium.	Iridium.	Platinum.	Gold.
190·3	192·5	194·3	196·8

The differences between the members of the same vertical series are thus:—

88·9	89·8	88·8	89·1

We propose to make further attempts to determine the chlorine in the palladammonium chloride and to ascertain the relation KCl : Pd in potassium palladious chloride. We, however, thought it desirable that the results already obtained should be published, and, indeed, we regard them as sufficient to establish the atomic weight, at any rate, with the degree of accuracy attainable in this group of elements. In conclusion, we must acknowledge valuable assistance from Mr. T. C. Moore, B.Sc., who carried out most of the preliminary investigations, but was unable to continue the work.

The Owens College,
Manchester.

LXVII.—*Resolution of Lactic Acid into its Optically Active Components.*

By T. Purdie, Ph.D., B.Sc., Assoc. R.S.M., Professor of Chemistry in the United College, University of St. Andrews, and J. Wallace Walker, M.A.

Van't Hoff relates, in the introduction to his *Chemistry in Space*, that the reflections which led him to his theory of the asymmetric carbon atom were suggested by the ideas of Wislicenus on the isomerism of lactic and sarcolactic acids, so that these acids may be said to have played a prominent part in the opening up of the new field of stereochemistry. It is noteworthy, in view of this fact, that only quite recently has experimental evidence been obtained that inactive lactic acid is actually composed of two oppositely active acids, as the theory referred to demands.

Lewkowitsch (*Ber.*, **16**, 2720) found that a solution of ammonium lactate became dextrogyrate under the action of *Penicillium glaucum*. Schardinger (Abstr., 1891, 666) obtained a lævolactic acid by the bacterial decomposition of cane sugar, the zinc salt of which crystallised with 2 mols. H_2O, like zinc sarcolactate, and showed that a mixture of these two salts in equal weights produced ordinary zinc lactate, which crystallises with 3 mols. H_2O.

While the work described in the present paper was being carried out, Linossier (*Ber.*, **24**, 660) published the results of a repetition and extension of Lewkowitsch's experiments on the action of *Penicillium glaucum* on lactic acid. Contrary to the experience of Lewkowitsch, he found that ammonium lactate became lævogyrate by the growth of the mould; from the ammonium salt he obtained a solution of a lævogyrate zinc salt, and from this a solution of a dextrogyrate acid.

These investigations, particularly that of Schardinger, prove conclusively that lactic acid consists of a dextro-acid, identical with sarcolactic acid, and of the lævogyrate isomeride, obtained as above from cane sugar. For the complete verification, however, of Van't Hoff and Le Bel's theory in the case of a common substance like lactic acid, it seemed to us desirable that direct analytical evidence of the composition of the acid should be supplied, and we therefore undertook the present investigation, the object of which was to resolve the substance in question into its constituent isomerides by the well-known methods discovered by Pasteur.

We find that the acid can, in fact, be decomposed into two oppositely active isomeric acids by means of the strychnine salt.

Preliminary Experiments.

Our first attempts were made with cinchonine. On dissolving this alkaloïd in an aqueous solution of lactic acid in the proportion requisite to form an acid salt, and evaporating, a jelly was formed which refused to crystallise. An aqueous solution of the acid in which cinchonine was dissolved to neutral reaction also left, on evaporation in a desiccator, a gelatinous residue, which did not crystallise from any of the usual solvents. On standing some days, however, radial bundles of fine prisms appeared, and ultimately the substance became a mass of minute crystals, imbedded in a viscid, dark-coloured gum. The crystals, being readily soluble in all the common solvents, were freed as far as possible from the uncrystallisable matter by pressure between folds of filter-paper. An aqueous solution of the substance, from which the cinchonine had been removed by precipitation with ammonia and then concentrated, gave a rotation of +0·3° when examined by the polarimeter in a 220 mm. tube. It appears, therefore, that the cinchonine salt of lævogyrate lactic acid is more readily crystallisable than its dextrogyrate isomeride, and that this difference in properties might possibly be utilised for the decomposition of lactic acid into its constituents. The effectual separation of the cinchonine salts, however, presented so much difficulty that the method was abandoned.

Experiments were also made with narcotine, but a crystalline salt of this alkaloïd could not be obtained.

Experiments made on a small scale with strychnine gave a more promising result, of which the following will serve as an example:—25 grams of the alkaloïd were treated with just the quantity of aqueous lactic acid to effect solution. When the liquid, which was only faintly acid, was evaporated and cooled, it became a thick paste of minute, prismatic crystals, which, when separated from the syrupy mother liquor by means of a suction pump and air dried, weighed 7·5 grams. The substance was dissolved in water, decomposed by the cautious addition of ammonia, and filtered; the filtrate, after being evaporated to 20 c.c., was again tested with ammonia, and gave no further precipitate of strychnine. It gave a rotation of +1·07° in a 220 mm. tube, whilst the mother liquor, containing the more soluble portion of the strychnine salt, when similarly treated, showed a rotation of −1·03°. When sodium carbonate was used instead of ammonia to remove the alkaloïd, the solutions of the sodium salts exhibited similar optical activity. When the ammonium salt solutions were digested with zinc oxide until ammonia was no longer evolved, much inactive zinc lactate crystallised out on cooling, but the remaining zinc salt solutions still showed dextro- and lævo-rotations respectively. On evaporating the solution of dextrogyrate zinc lactate, a considerable quantity of zinc salt crystallised in needles, and the syrupy liquid then deposited comparatively large, well formed, transparent prisms, exhibiting also a dextrorotation. These crystals were found to contain both zinc and ammonia, and subsequent analysis proved them to be a zinc ammonium salt of definite composition. The concentrated solution of the lævogyrate zinc salt also deposited crystals exactly similar in appearance, mixed, however, with much larger quantities of inactive zinc lactate.

Further experiments showed that the amount of strychnine salt which crystallised depended only on the extent to which the solution was evaporated, and that when the salt which was first deposited was recrystallised, though reduced by the process to half its weight, it nevertheless yielded a more optically active liquid when decomposed. It thus appeared that the strychnine salts of both acids were crystallisable, that which yielded the lævogyrate salts (presumably sarcolactates) being, however, the more soluble of the two, and that, consequently, the solutions obtained from the strychnine salts were mixtures respectively of dextro- and lævo-, with probably larger quantities of inactive lactate. It was, therefore, evident that systematic crystallisation of the strychnine salt would be required in order to separate the two active acids.

The lactic acid used in our experiments was the syrup (sp. gr. 1·21) prepared by Kahlbaum. When examined in the polarimeter in the concentrated form, and also when diluted with an equal volume of water, no activity could be detected. By titration with standard alkali according to Wislicenus' method (*Annalen*, **164**, 184), we found that the solution contained 55·9 per cent. of lactic acid and 31·1 per cent. of the monobasic anhydride. The quantity of strychnine required to make a neutral solution indicated that the anhydride was not decomposed into lactic acid by the alkaloïd. In order to avoid complications arising from this fact in the larger experiments to be described, we took the precaution of boiling the acid syrup after dilution with water to ten times its volume, until all the anhydride was converted into acid.

Wislicenus (*Annalen*, **164**, 182, 196) showed that monobasic lactic anhydride is readily converted into lactic acid by alkalis, although it may be left for a long time in contact with water at the ordinary temperature without undergoing complete conversion. We find no precise data regarding the conditions under which the anhydride is converted into acid by heating with water, so the following results may be mentioned. A series of separate experiments showed that when the syrup, containing 31·1 per cent. by weight of the anhydride, was diluted to ten times its volume with water and boiled, using a reflux condenser, the quantity of anhydride, calculated on the weight of syrup taken, was reduced in half an hour to 23·6 per cent., in 1½ hours to 16·3 per cent., and, after six hours boiling was entirely converted into acid.

Larger Experiments with Strychnine.

460 grams of strychnine were dissolved in just the quantity of lactic acid required for solution, namely, 1350 c.c. of a solution of the acid prepared as above. The solution was neutral, and the acid and alkaloïd, it was found on calculation, had acted in almost molecular proportion. The liquid was then subjected to systematic fractional crystallisation, the crystalline solid being in each case separated, as far as practicable, from the syrupy liquid with the aid of the suction pump, and pressed in folds of filter-paper. The compound readily gave off water when heated, and no definite melting point could be obtained; but with successive crystallisations the solubility of the separated substance decreased very decidedly. Ultimately three crops of crystals and seven mother liquors were obtained. The three crops of crystals, C_1, C_2, and C_3, in order of increasing solubility, had been crystallised respectively five, six, and seven times, their respective weights, air dried, being 61·5, 22, and 31·5 grams. The crops of crystals were dissolved separately in water, and the strychnine was precipitated by the addition of ammonia in very slight excess. The filtrates were evaporated to a small bulk, again neutralised with ammonia, and allowed to stand, any small quantity of strychnine which separated being filtered off. The solution from C_1 was made up to 50 c.c., and the other two solutions to such volumes that all three were of the same concentration. The three solutions in order gave the following rotations in a 200 mm. tube: $+5{\cdot}46°$, $+4{\cdot}83°$, and $-1{\cdot}33°$.

Lævolactic Acid.

The composition and chemical properties of this acid and its salts should from all analogy be identical with those of sarcolactic acid (dextrolactic acid). As among the few sarcolactates which have been investigated with any degree of accuracy, the zinc compound is the best known and best characterised, our experiments with the optically active lactic acids have been for the present chiefly confined to this salt. Besides the well-established difference in the amount of water of crystallisation of zinc sarcolactate and ordinary zinc lactate, the investigations of Wislicenus have shown that the former is about three times as soluble in water as the latter, and the same ought to hold true of course for zinc lævolactate.

Zinc Lævolactate.—With the view of obtaining this salt, the dextrogyrate ammonium salt solution from C_1 was boiled with zinc oxide until ammonia had almost ceased to be evolved, and then filtered and evaporated. Three crops of crystals were obtained weighing respectively 9·7, 5, and 1·1 grams; the first proved to be the approximately pure zinc salt of lævolactic acid, the second the same substance mixed with more inactive zinc lactate, and the third, which crystallised in large and well-defined crystals, a double zinc ammonium salt.

The zinc salt, weighing 9·7 grams, was recrystallised, dried between folds of filter-paper, and then subjected to analysis and examined by the polarimeter with the results which are appended below. The water of crystallisation was estimated by heating the salt in a platinum crucible at 105° until absolutely constant in weight; it was found that no further loss was undergone by heating it to 180°. The zinc was estimated by careful incineration.

I. 0·6605 gram of substance heated at 105° lost 0·0875 gram, and yielded 0·1908 gram ZnO.

II. 0·6943 gram of substance heated at 105° lost 0·0915 gram.

III. 0·2998 gram of the residual salt from II gave on combustion in oxygen 0·1130 gram H_2O, 0·3221 gram CO_2, and 0·0994 gram ZnO.

IV. 0·2955 gram of the residual salt from II gave on combustion in oxygen 0·1087 gram H_2O and 0·3180 gram CO_2.

	Calculated for $C_6H_{10}O_6Zn,2H_2O$.	Found. I.	Found. II.
H_2O......	12·90	13·25	13·18
Zn	23·30	23·18	—

	Calculated for $C_6H_{10}O_6Zn$.	Found. III.	Found. IV.
C	29·63	29·30	29·35
H	4·12	4·19	4·09
Zn......	26·75	26·61	—

As a control experiment, a specimen of zinc salt was prepared from the original lactic acid by treating it with zinc oxide, and a portion of the salt was heated in the air-bath at 105° simultaneously with the optically active salt the analysis of which is given above.

0·7017 gram of the substance lost 0·1276 gram H_2O, and yielded on incineration 0·1918 gram ZnO.

	Calculated for $C_6H_{10}O_6Zn,3H_2O$.	Found.
H_2O	18·18	18·18
Zn........	21·89	21·93

In determining the specific rotation of the active zinc salt, 1·9240 gram was dissolved in water and the solution made up to 20·06 c.c., and the following results obtained :—

$$\alpha[11°] = +1·08°;\ l = 200\text{ mm.};\ C = 9·591;\ d\ 11°/4° = 1·0449;$$

hence

$$[\alpha]_D = \frac{1·08 \times 100}{2 \times 9·591} = +5·63°.$$

The zinc salt made direct from the original lactic acid was inactive. The polarimeter used throughout in our experiments was a half-shadow instrument of the Laurent form, admitting of readings to single minutes.

The analyses given show that the zinc lævolactate has the same composition as zinc sarcolactate. The estimations of the water of crystallisation are slightly higher than the calculated numbers, and indicate that the substance was not free from inactive salt, which is also confirmed by the specific rotation. The specific rotation of zinc sarcolactate varies with the concentration; the number found by Wislicenus for this salt (*Annalen*, **167**, 332) for a strength of solution approximating to that we used was −6·36°. If the quantity of inactive salt probably present be calculated from the estimation of water of crystallisation, and a corresponding allowance made, then the specific rotation would approach pretty closely to the number found by Wislicenus.

Owing to the facility with which the zinc lactates form supersaturated solutions, estimations of solubility vary within wide limits according to the length of time the solutions are allowed to stand. Wislicenus states (*loc. cit.*) that the solubilities of zinc lactate and sarcolactate at 14—15° may be taken respectively as about 1·7 and 5·7 parts hydrated salt in 100 parts of water. We made comparative experiments on the solubility of ordinary zinc lactate and the zinc lævolactate, described above, by dissolving 2 grams of each in 15 c.c. of water with the aid of heat, and then leaving the solutions to stand close together for about 6 weeks, the temperature varying from 10° to 18°. 6·2970 grams of the solution of the active salt left on evaporation and incineration of the residue 0·0878 gram ZnO, whilst 5·2733 grams of solution of the inactive salt gave 0·0229 gram ZnO; the solubilities of the hydrated salts are, therefore,

Inactive zinc lactate........	1·62 : 100
Zinc lævolactate............	5·05 : 100

results which agree as closely with the numbers quoted above as could be expected. The solubility of zinc lævolactate, therefore, is the same as that of the sarcolactate.

As a determination of the water of crystallisation in the second crop of crystals, weighing 5 grams, gave the number 14·45 per cent., it evidently contained more inactive salt than the first crop, and it seemed, therefore, unlikely that a purer salt would be got by recrystallisation.

Zinc Ammonium Lævolactate.—We found this salt, as already stated, in the mother liquor of the zinc lævolactate, the boiling with zinc oxide not having sufficed to decompose the whole of the ammonium salt. As the substance formed comparatively large well-defined crystals, and no corresponding compound of inactive lactic acid seemed to have been observed, we prepared the salt with the view of procuring from it, if possible, a lævolactate free from inactive salt.

1·1 gram of the salt was got, as already stated, from the mother liquor of the zinc lævolactate, the analyses and specific rotations of which have been given. A second portion of 2·25 grams was obtained by decomposing with zinc oxide half of the ammonium salt from the crop of strychnine lactate C_2, and adding the zinc lævolactate thus obtained to the remaining half of the ammonium salt solution. A third portion of 3 grams was prepared by decomposing one half of the residue of the zinc lævolactate, the analyses of which have been given, with sulphuretted hydrogen, neutralising the resulting acid with ammonia, and adding this to the remaining half of the zinc salt.

These solutions were evaporated to a syrupy consistency without any zinc salt crystallising, but on adding a crystal of zinc ammonium salt, transparent, short, well-defined prisms were at once produced. The substance having been freed from adhering syrup by means of filter paper was subjected to analysis with the following results:—

I. 0·7920 gram of substance gave 0·1655 gram ZnO.

II. 0·3157 gram of substance gave 0·1752 gram H_2O, 0·3222 gram CO_2, and 0·0668 gram ZnO.

III. 0·2883 gram of substance gave 0·1582 gram H_2O, 0·2955 gram CO_2, and 0·0605 gram ZnO.

0·2840 gram of substance gave by combustion 9·2 c.c. N. at 14° and 750·1 mm. bar.

	Calculated for $C_9H_{15}O_9Zn\cdot NH_4,2H_2O$.	Found. I.	Found. II.	Found. III.
C	27·98	—	27·83	27·95
H	5·96	—	6·07	6·10
N	3·63	—	—	3·82
Zn......	16·84	16·77	16·98	16·84

The substance is, therefore, a double lactate of zinc and ammonium crystallising with 2 mols. H_2O. A direct estimation of the water of crystallisation was not obtained, as ammonia was given off when the substance was heated. The salt is readily soluble in water, but cannot be recrystallised; on warming the solution, or even on evaporation at the ordinary temperature, it becomes acid from escape of ammonia, and zinc salt is gradually deposited. When excess of the ammonium salt, however, is present, a supersaturated solution may be produced by evaporation without the separation of zinc salt taking place.

Determinations of the specific rotation gave the following results:—

$$\text{I. } \alpha[13^\circ] = +0{\cdot}89^\circ;\ l = 200\text{ mm.};\ p = 7{\cdot}7804;\ d\ 13^\circ/4^\circ = 1{\cdot}0313;\ \text{hence } [\alpha]_D = \frac{0{\cdot}89 \times 100}{2 \times 7{\cdot}7804 \times 1{\cdot}0313} = +5{\cdot}54^\circ.$$

$$\text{II. } \alpha[11^\circ] = +1{\cdot}02^\circ;\ l = 200\text{ mm.};\ p = 8{\cdot}6225;\ d\ 11^\circ/4^\circ = 1{\cdot}0364;\ \text{hence } [\alpha]_D = \frac{1{\cdot}02 \times 100}{2 \times 8{\cdot}6225 \times 1{\cdot}0364} = +5{\cdot}71^\circ.$$

$$\text{III. } \alpha[18^\circ] = +1{\cdot}16^\circ;\ l = 200\text{ mm.};\ p = 8{\cdot}6305;\ d\ 18^\circ/4^\circ = 1{\cdot}0350;\ \text{hence } [\alpha]_D = \frac{1{\cdot}16 \times 100}{2 \times 8{\cdot}6305 \times 1{\cdot}0350} = +6{\cdot}49^\circ.$$

$$\alpha[18^\circ] = +0{\cdot}85^\circ;\ l = 200\text{ mm.};\ p = 5{\cdot}8669;\ d\ 18^\circ/4^\circ = 1{\cdot}0240;\ \text{hence } [\alpha]_D = \frac{0{\cdot}85 \times 100}{2 \times 5{\cdot}8669 \times 1{\cdot}0240} = +7{\cdot}07^\circ.$$

The specific rotations of I, II, and III were taken on different preparations of the salt. The two determinations on Preparation III, which was, no doubt, the purest, show that the specific rotation increases with decreasing concentration, as is the case with zinc sarcolactate. The specific rotations found for II and III indicate that these substances still contained some inactive salt, whether mixed or chemically combined with the active constituents, it is impossible to say. Inactive zinc and ammonium lactates do not seem to form any compound similar to that which has been described. The methods by which the active compound was prepared yielded no crystalline double salt when inactive salts were used. A dilute, hot solution of the latter deposits zinc lactate on cooling; a warm, concentrated solution of ammonium lactate will dissolve large quantities of zinc lactate, which the syrup still retains in solution on cooling, but on longer standing, or with stirring, zinc lactate separates.

The remaining portion of Preparation III of the zinc ammonium salt was converted into the zinc salt, with the view of obtaining a purer specimen of this substance. The zinc was removed as far as possible, by means of sulphuretted hydrogen, and the ammonia then driven off by heating the filtered solution with a slight excess of barium hydrate. Sulphuric acid was added in quantity nearly equivalent to the barium hydrate used, and the filtered solution evaporated to a syrup, and extracted with ether. After evaporating off the ether, the acid was dissolved in water, and converted into the zinc salt in the usual manner. A determination of the specific rotation is appended:—

$$\alpha[17^\circ] = +0{\cdot}88^\circ;\ l = 200 \text{ mm.};\ p = 6{\cdot}7510;\ d\ 17^\circ/4^\circ = 1{\cdot}0318;\ \text{hence } [\alpha]_D = \frac{100 \times 0{\cdot}88}{2 \times 6{\cdot}7510 \times 1{\cdot}0318} = +6{\cdot}32^\circ.$$

This result is still considerably lower than that found by Wislicenus with solutions of zinc sarcolactate of similar concentration. An estimation of the water of crystallisation in another portion of the salt gave the result 13·30, the number calculated for $2H_2O$ being 12·90.

Lævolactic Acid.—The activity of sarcolactic acid is in the opposite sense to that of its salts. The same holds true for lævolactic acid. A solution of zinc salt, which gave a rotation of +1·08° in a 200 mm. tube, was decomposed with sulphuretted hydrogen, filtered, and made up to the same volume, when it was found to give a rotation of −0·27°.

Like sarcolactic acid, lævolactic acid readily forms an anhydride, the activity of which is in the opposite sense to that of the acid. The solution just referred to was evaporated, and the acid separated from a small quantity of undecomposed zinc salt by extraction with ether. The syrup left from the ethereal extract was dissolved in water just sufficient to fill a 100 mm. tube; it was inactive. After standing three weeks, and being diluted so as to fill a 200 mm. tube, it gave the original rotation −0·27°.

Dextrolactic Acid.—It has been already stated that of the three crops of crystals of strychnine salt, the first and second yielded a dextrogyrate, the third a lævogyrate ammonium salt. The weight of the first two crops together amounted only to about 14½ per cent. of the weight of acid and alkaloïd used, so it was evident that the mother liquors must contain, besides the salt of the dextro-acid, a large quantity of the salt of the lævo-acid, the elimination of which was only to be effected by fractional crystallisation. As the process proved extremely tedious, and offered little promise of success, it was ultimately abandoned, and the various mother liquors, without further separation of the mixed salts, were decomposed separately by the addition of barium hydrate. The filtered solutions, from which the excess of barium hydrate had been removed by carbonic anhydride, were next concentrated to a small bulk, and, after standing, again filtered from small quantities of the alkaloïd, which separated. Each of the solutions gave, as was expected, a lævo-rotation. They were then mixed together, and treated with slightly less than the quantity of standard sulphuric acid requisite to precipitate the barium. The filtered liquid was evaporated to a syrup, from which the lactic acid was extracted with ether. The residue from the ethereal extract, after evaporation, was dissolved in water, and converted into a solution of the zinc salt in the usual manner, from which, on cooling, large quantities of inactive zinc lactate separated.

Zinc Dextrolactate.—By successive crystallisations of the liquid mentioned, and extraction of the more soluble part of the various crops of crystals, a solution was ultimately obtained which yielded two portions of crystals weighing $2\frac{1}{2}$ grams and 1·9 grams respectively.

The following analyses and determinations of specific rotation showed them to consist mainly of zinc dextrolactate :—

0·4178 gram of the first crop, on heating at 105° till constant in weight, lost 0·0566 gram, and yielded 0·1209 gram ZnO, corresponding to 13·55 per cent. of water, and 23·22 per cent. of zinc, instead of the numbers 12·90 and 23·29 calculated for the salt containing $2H_2O$.

A determination of the specific rotation was made, with the following result :—

$$\alpha[16°] = -1{\cdot}01°;\ l = 200\text{ mm.};\ p = 9{\cdot}1351;\ d\ 16°/4° = 1{\cdot}0427;\ \text{hence } [\alpha]_D = \frac{100 \times -1{\cdot}01}{2 \times 9{\cdot}1351 \times 1{\cdot}0427} = -5{\cdot}32°.$$

The second crop proved to be purer, as is shown by the specific rotation :—

$$\alpha[18°] = -1{\cdot}08°;\ l = 200\text{ mm.};\ p = 9{\cdot}0823;\ d\ 18°/4° = 1{\cdot}0413;\ \text{hence } [\alpha]_D = \frac{100 \times -1{\cdot}08}{2 \times 9{\cdot}0823 \times 1{\cdot}0413} = -5{\cdot}71°.$$

The specific rotation found for a solution of the dextrogyrate zinc salt of similar concentration was +5·63°.

Zinc Ammonium Dextrolactate.—This salt was prepared by the same methods, which yielded the corresponding salt of the lævo-acid. It crystallised in the same manner from supersaturated solutions, and had the same chemical composition. An estimation of zinc gave 16·92 per cent., the calculated percentage being 16·84. The solution from which the salt was prepared was known to contain a considerable amount of inactive substance, and, as our experience with the corresponding salt of the lævo-acid led us to expect, the specific rotation was low. The number was $-6·28°$, that for the purer lævolactate of similar concentration being $+7·07°$.

Dextrolactic Acid.—The lævogyrate zinc salts, which have been described, yielded, as was expected, a dextrogyrate acid. The acid obtained from a lævogyrate barium salt solution made up to 13 c.c. gave a rotation of $+0·27°$. When this acid was converted into zinc salt, and the solution made up to 25 c.c., it exhibited a rotation of $-0·58°$.

Confirmatory Experiments.

The following experiment was made to show that, when lactic acid is resolved into its optically active isomerides by means of their strychnine salts, the quantities of the latter which are separated from each other possess equal optical activity. 70 grams of lactic acid syrup were converted into a solution of strychnine salt, as already described, and from this a crop of crystals was obtained by evaporation. The crystalline strychnine salt and its mother liquor were converted into their barium salts by barium hydrate, and the liquids were shaken with chloroform to remove any strychnine which remained. As the solutions were too highly coloured for examination, they were diluted to 250 c.c. The rotations then exhibited in a 200 mm. tube were $+0·45°$ and $-0·45°$ respectively.

Our experiments show that inactive lactic acid can be resolved into two optically active isomeric acids, the zinc salts of which both crystallise with 2 mols. H_2O. By mixing equal weights of these in solution, inactive zinc lactate, crystallising with 3 mols. H_2O, should be produced. We find that this is in fact the case. We dissolved separately 1·2 gram each of the dextro- and lævo-gyrate zinc salts from our purest preparations, of which the estimations of water and specific rotation have been given, in such quantities of water as to form saturated solutions. No salt separated from the liquids on standing some hours, or on stirring. But when the solutions were mixed at the ordinary temperature and stirred, the liquid became turbid almost instantaneously, and in a few minutes a heavy precipitate of crystalline needles subsided, which, on being separated and dried, weighed over 1 gram. A saturated solution of the crystals was found to be absolutely inactive, and the composition of the substance was identical with that of ordinary zinc lactate.

0·8925 gram lost at 105° 0·1626 gram H_2O, and yielded on incineration 0·2434 gram ZnO.

	Calculated for $C_6H_{10}O_6Zn,3H_2O$.	Found.
H_2O	18·18	18·22
Zn..........	21·89	21·88

Our experiments show that fermentation lactic acid can be resolved into two oppositely active acids, one of which is identical with sarcolactic acid, the other with the lævorotatory acid produced, as already referred to, by the bacterial decomposition of cane sugar.

LXVIII.—*Some Homonucleal Tri-derivatives of Naphthalene.*

By RAPHAEL MELDOLA, F.R.S., and C. H. DESCH.

WHEN parabromo-α-acetonaphthalide is nitrated in acetic acid solution, it readily forms a homonucleal mononitro-derivative (Liebermann and Scheiding (*Annalen*, **183**, 258). The nitro-group is ortho- to the acetamido-group in this compound, as is shown by its yielding an anhydro-base on reduction (Meldola, Trans., 1885, **47**, 505).* The nitrobromo-α-acetonaphthalide is easily and quantitatively hydrolysed into the nitrobromo-α-naphthylamine,

$$NH_2 : NO_2 : Br = 1 : 2 : 4,$$

by means of sulphuric acid (*ibid.*, p. 500).

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* At the time of the researches above referred to, I was led to the conclusion that when the mixed nitro-derivatives obtained by nitrating α-acetonaphthalide in acetic acid (Liebermann's method) are brominated, it is the paranitro-compound only which is attacked. This conclusion was based on a supposed isomerism of the nitrobromo-derivative, which apparently differed in melting point from Liebermann's. But the isomerism was more especially inferred from the observation that the dibromonaphthylamine obtained from this compound by hydrolysis, replacement of NH_2 by H, reduction, acetylation, bromination, and hydrolysis gave a bromophthalic acid by oxidation (*loc. cit.*, p. 511). Liebermann and Scheiding's compound by similar treatment gave a dibromonaphthylamine which gave doubtful results on oxidation (*loc. cit.*, p. 515). Both dibromonaphthylamines gave the same dibromonaphthalene by the diazo-reaction. I had always intended to repeat these experiments in order to clear up the discrepancy, but as my colleague, Dr. Armstrong, was engaged in a detailed study of the naphthalene derivatives with a view to settle the

Some years ago experiments were commenced by one of the authors of this note with the object of ascertaining whether in homonucleal tri-derivatives the hydrogen in the second β-position could be substituted by NO_2, so as to produce homonucleal tetra-derivatives from which the missing di-β-quinone might possibly be prepared. It was thought that if the quinone itself could not exist, its di-haloïd derivatives of the type $C_{10}H_4Br_2O_2$ [Br : O : O : Br = 1 : 2 : 3 : 4] might be more stable. The discovery of tetrabromo- and tetrachloro-ortho-benzoquinone by Zincke in 1887 (*Ber.*, **20**, 1776) gave encouragement to continue the work in this direction. As a preliminary step, it was attempted to replace the amido-group in the nitrobromonaphthylamine by bromine by decomposing the diazo-perbromide, $C_{10}H_5Br(NO_2)\cdot N_2\cdot Br_3$, in the usual way. It was found, however, that by this method the nitro-group was also replaced by bromine, and the product consisted only of the tribromonaphthalene (m. p. 113—114°) previously described by one of us (Trans., 1883, **43**, 4). About the same time, and quite independently, the same result was announced by Prager (*Ber.*, 1885, **18**, 2163). This author further stated in his paper that the amido-group in the nitrobromonaphthylamine could not be replaced by bromine by Sandmeyer's modification of the diazo-reaction. Accepting Prager's statement as correct, the experiments were accordingly abandoned.

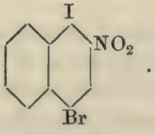
orientation of the substituents in the di- and tri-chloro and di- and tribromo-derivatives, this field was left to him. In a recent communication by Armstrong and Rossiter (Proc., No. 104, **7**, 186), these authors have shown that the product of the action of bromine on the mixed nitro-α-acetonaphthalides is identical and not isomeric with Liebermann and Scheiding's compound, and that it is therefore the ortho- and not the para-compound which is attacked, as I had originally supposed. They have also shown that the two bromonaphthalenes are identical, being the 1 : 4-modification (m. p. 82—83°). These results, which I have since repeated with the assistance of Mr. E. M. Hawkins, and can now corroborate, are instructive as enforcing the conclusion to which I was led seven years ago, that in the study of isomeric naphthalene derivatives, melting points are of little or no value (*loc. cit.*, p. 516). All subsequent experience has confirmed this. It appears also that oxidation with nitric acid gives very uncertain information respecting the homo- or heteronucleal character in many cases. These and other difficulties which the investigator of naphthalene derivatives has to guard against are pointed out by Armstrong and Rossiter in another note (Proc., No. 104, **7**, 182). The effect of the revision of the work by these authors is to remove my bromonaphthylamine (m. p. 62°) and its derived compounds from the list of naphthalene derivatives. I am glad of the present opportunity of preventing the perpetuation of these compounds in chemical literature. I may also take occasion to remark that the 1 : 1′-(peri)dibromonaphthalene which formed the object of the investigation by Armstrong and Rossiter referred to above has recently been obtained by me in conjunction with Mr. F. W. Streatfeild from the 1 : 1′-nitronaphthylamine. The melting point of peri-dibromonaphthalene is 108·5—109°. Details concerning this and other peri-di-derivatives will be given when our investigations are more complete.—R. M.

Having recently had occasion to prepare a quantity of the nitrobromonaphthylamine, it appeared worth while to try whether a feebler acid like iodhydric acid would enable the NH_2 group to be replaced by iodine, without at the same time replacing the NO_2 group. The nitrobromonaphthylamine was dissolved in strong sulphuric acid, the solution diluted with a little water, and when cold diazotised in the usual way. The solution of the diazo-salt was filtered into a solution containing the calculated quantity of potassium iodide. Decomposition occurs at ordinary temperatures with the evolution of nitrogen, and the reaction is completed by gently heating for some time till no more gas is evolved. The resinous-looking product was washed with water, and then crystallised repeatedly from alcohol with the addition of animal charcoal. The purified compound consisted of small, ochreous needles, melting at 117—118°. Analysis showed that the desired substitution had taken place:—

0·4819 gram gave 15·3 c.c. moist N at 15·6 and 764·9 mm. bar.
0·2982 „ 0·3344 gram mixed AgBr and AgI.

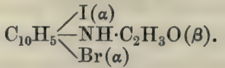
	Calculated for $C_{10}H_5IBr{\cdot}NO_2$.	Found.
N..............	3·70	3·73
Br + I..........	54·76	54·87

The constitution of this nitrobromoiodonaphthalene is:—



The substance is very readily soluble in benzene, but slightly soluble in petroleum, and freely soluble in hot alcohol, acetone, and glacial acetic acid. By the action of zinc-dust and acetic acid, the compound can be reduced in alcoholic solution, without the removal of halogen, if the solution is kept cool. The base, bromoiodo-β-naphthylamine, is thrown out of the alcoholic solution on dilution with water, in the form of whitish needles, melting when crude at about 89°. The substance soon becomes reddish-brown by oxidation on exposure to the air, and has not therefore been isolated in a state of purity. Its basic character is practically destroyed by the halogen atoms present in the molecule. The acetyl derivative was prepared by heating the solution of the compound in glacial acetic acid with acetic anhydride. After several crystallisations from alcohol, the pure bromoiodo-β-acetonaphthalide was obtained in the form of opaque, white needles, melting at 235°:—

0·2277 gram gave 7·1 c.c. moist N at 20° and 761 mm. bar.

	Calculated for  $C_{10}H_5\begin{matrix}\diagup I(\alpha)\\ -NH\cdot C_2H_3O(\beta).\\ \diagdown Br(\alpha)\end{matrix}$	Found.
N	3·59	3·57

The direct replacement having been so easily effected in the case of iodhydric acid, we were led to repeat Prager's work, using Sandmeyer's method. In the first place, the solution of the diazotised nitrobromonaphthylamine was filtered into an excess of cuprous chloride solution, and the reaction completed by heating in the usual manner. The crude product was crystallised several times from alcohol, and finally obtained in the form of ochreous needles, melting at 117°, and possessing all the properties of the preceding compound. A qualitative test showed the presence of nitrogen. Analysis gave the following results:—

0·2922 gram gave 13·7 c.c. moist N at 21° and 759·5 mm. bar.
0·1955 ,, 0·2257 gram mixed AgCl and AgBr.

	Calculated for $C_{10}H_5ClBr\cdot NO_2$.	Found.
N	4·89	5·33
Cl + Br	40·32	40·22

The compound can be reduced in cold alcoholic solution with zinc-dust and acetic or even hydrochloric or sulphuric acid, without loss of halogen. The amido-derivative, which is possessed of but very feeble basic properties, separates from the alcoholic solution on dilution with water, in the form of whitish needles. Although somewhat more stable than the corresponding bromoiodo-β-naphthylamine, it also becomes coloured by oxidation on exposure to the air, and has not been obtained as yet in a pure state. A specimen crystallised two or three times from benzene was obtained in the form of brownish, stumpy needles, melting at about 93°. We do not give this melting point as final, as it is proposed to prepare a larger quantity of the substance for future extension of the work. Analysis showed, however, that even at this stage the compound was fairly pure:—

0·1756 gram gave 8·4 c.c. moist N at 18·5° and 766·8 mm. bar.

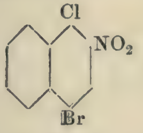
	Calculated for $C_{10}H_5ClBr\cdot NH_2$.	Found.
N	5·46	5·56

The acetyl derivative was prepared by acetylating in acetic acid with acetic anhydride. After several crystallisations from dilute alcohol, it formed fine, white needles, melting at 218° :—

0·1474 gram gave 5·9 c.c. moist N at 18° and 765·2 mm. bar.

	Calculated for $C_{10}H_5ClBr{\cdot}NH{\cdot}C_2H_3O$	Found.
N	4·69	4·65

By a similar application of Sandmeyer's method, the nitrobromonaphthylamine was converted into dibromonitronaphthalene, which, when pure, forms small, ochreous needles, melting at 117°. The constitution of these last compounds is represented by the formulæ :—



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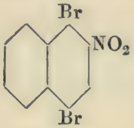

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The results now submitted are sufficient to show that Prager was in error in stating that Sandmeyer's method is inapplicable to the nitrobromonaphthylamine in question. It is proposed to extend the investigation of these compounds in the direction indicated at the outset, and the present note is offered as a preliminary communication, owing to unadvoidable interruption of the work till the autumn.

Finsbury Technical College.

LXIX.—*A Method of Measuring the Vapour Pressures of Solutions.*

By Thomas Ewan, B.Sc., Ph.D., 1851 Exhibition Scholar in Chemistry at the Owens College, and W. R. Ormandy, Bishop Berkeley Fellow in Chemistry at the Owens College.

In a note in the *Compt. rend.* for 1890, **111**, 102, M. G. Charpy has pointed out that a condensation hygrometer, such as Regnault's, may be advantageously used for determining the vapour pressures of aqueous solutions at ordinary temperatures. The same suggestion is made by Ostwald (*Lehrbuch der Allgemeinen Chemie*, 2te Aufl., Band I, 715).* Having occasion to make some determinations of molecular weights in aqueous solutions at the ordinary temperature, we decided to employ this method, and as it appears to be of some practical utility, we publish our results so far as they have gone.

---

* Since writing this our attention has been drawn to the work of H. Lescœur (*Ann. Chim. Phys.* [6], **16**, 394, 1889). He has used the method for the determination of the pressure of dissociation of hydrated salts.

The apparatus which we used is represented in Fig. 1.

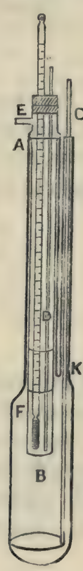


FIG. 1.

The glass vessel AB, which contains the solution under examination, consists of a cylindrical bulb 13 cm. long and 4·5 cm. in diameter, with a narrower neck, 20 cm. long and 2 cm. in diameter. A narrow side tube is sealed (at K) into the shoulder of the bulb, through which the stirrer C passes. This consists of a ring of stout platinum wire, sealed to a light glass handle. The platinum ring just touches the sides of the vessel B, so that they can be kept moistened with the solution.

The hygrometer EF consists of a thin polished silver cup F, soldered to a stronger ring of brass, which in its turn is joined to a glass tube ED. This joint was made by slipping the glass tube inside the brass one, packing the space between them with thin tin foil, and then pouring in melted sulphur. The joint was quite impervious to ether, and by occasionally heating it to the melting point of the sulphur it may be kept quite tight. The upper end of the hygrometer tube at E is closed with a cork, through which pass a thermometer and an open tube, carried down below the surface of the ether in the usual way. A side tube at E is connected with an aspirator in such a way that the amount of air passing through the ether is under the control of the observer. The hygrometer slips loosely through the tube AK, and is supported by an enlargement at A. The whole apparatus was immersed in a water-bath holding about 16 litres, and provided with glass windows back and front. The arrangements for keeping it at a constant temperature were very similar to those described by Ostwald (*Zeit. physikal. Chem.*, **2**, 565, 1888). The stirrer was kept in motion by means of a small water-motor. The temperature of the bath seldom varied as much as 0·1° C. in a day.

The temperatures of the bath and of the ether in the hygrometer were read on two thermometers by Hicks, graduated in 1/10 degrees. As each division was about $1\frac{1}{2}$ mm. wide, 1/100 degree could be estimated with certainty.

One of the thermometers (69) was correct at zero; its readings were accepted as correct, and the readings of the other thermometer (70) corrected so as to agree with it. The corrections used were at 21°, −0·076; 18°, −0·024; 15°, +0·010.

These numbers are the means of a number of comparisons; a curve was drawn from them, and the corrections to be applied at other temperatures obtained from it.

The experiments were carried out as follows:—The vessel B was cleaned by filling it with a mixture of sulphuric acid and potassium dichromate, and allowing it to stand over night; it was then washed with water and dried, and 30 to 40 grams of carefully distilled water were weighed into it, from a pipette of the form used by Beckmann (*Zeit. physikal. Chem.*, **4**, 548, 1889). The salt was also weighed into B from a tube bent at right angles, so that none of the salt adhered to the neck, AK. This precaution is of some importance, as the hygrometer has to be frequently slipped in and out of the vessel. The solution being made up, the whole apparatus is placed in position in the water-bath, and allowed to stand for about 15 minutes, till the air inside becomes saturated with vapour. With dilute solutions this time is ample, but with concentrated solutions we have sometimes observed a small rise in the dew point on standing somewhat longer, owing, doubtless, to the air not being at first fully saturated.

The readings of the dew point were made by simply observing the temperature at which dew first became visible on the hygrometer. We found by a number of preliminary observations that the readings can be made more accurately in this way (when certain precautions are taken) than by the ordinary method. The silver cup of the hygrometer was illuminated by means of a lamp and lens, placed 2 or 3 feet behind the observer. The silver surface is looked at through a biconvex lens of small focal length, the eye being in such a position that the light from the lamp is not reflected directly into it.

The dew point being approximately known, the temperature of the ether is lowered rapidly, till it is only one- or two-tenths of a degree above the point required, after which it is allowed to sink very slowly. When the dew point is reached, the surface of the silver becomes covered with fine white lines and scratches. After a little practice, the point at which these first appear can be read with certainty. The surface of the silver must be kept very clean. Spots of grease, dirt, &c., which are invisible in the air become visible as whitish patches on the silver before the dew point is reached, and may lead to too high a reading. We found that the tube could be kept sufficiently clean by means of clean dry wash leather and fine jewellers' rouge.

The numbers given in the tables for each solution are the means of three or four readings of the dew point. The greatest difference between two readings was never more than 0·1°; as a rule it was 0·02° or 0·03°.

In order to test the accuracy of our method of reading the dew point, we made a number of determinations of the dew point with pure water. It should of course be exactly the temperature of the bath. The following are the numbers obtained:—

Temp. of bath.	Dew point.	Diff.
18·30	18·30	0·00
18·30	18·29	−0·01
18·29	18·27	−0·02
18·30	18·30	0·00
18·39	18·39	0·00
18·40	18·42	+0·02
18·41	18·42	+0·01

The following tables contain the results obtained with sodium chloride solutions. The letters used have the following significations:—

c = gram molecules of NaCl in 1000 grams of water.
t = temperature of the solution.
t' = dew point.
f' = vapour pressure of water at the temperature t'. (It is also the vapour pressure of the solution at t.)
f/f' is the ratio of the vapour pressure of water to that of the solution, both at $t°$.

The values of f and f' corresponding to the temperatures $t°$ and $t'°$, are taken from the table of vapour pressures for each tenth of a degree calculated by Regnault (*Mém. de l'Acad.*, **21**, 627, 1847) from his formula D.

TABLE I.—*Sodium Chloride.*

c.	*t.*	*t′.*	*f′.*	*f/f′.*
0·485	20·990	20·718	18·179	1·017
1·047	21·000	20·353	17·775	1·041
1·536	21·018	20·159	17·564	1·054
2·660	21·046	19·504	16·865	1·100
3·044	21·002	19·137	16·487	1·122
4·407	21·000	17·937	15·299	1·209
5·162	21·000	17·281	14·679	1·260
5·307	20·975	16·751	14·197	1·301
0·583	18·103	17·796	15·163	1·019
1·367	18·090	17·382	14·772	1·045
1·564	18·122	17·237	14·639	1·057
2·567	18·025	16·786	14·228	1·081
4·091	18·190	15·480	13·095	1·187
5·292	18·238	14·528	12·320	1·265
0·284	14·825	14·691	12·451	1·009
1·524	14·985	14·147	12·023	1·055
4·852	14·977	11·731	10·276	1·234

As solutions of NaCl follow von Babo's law with close approximation, we have assumed the values of *f/f′* observed at temperatures differing slightly from 21°, 18°, and 15° to be the true values at these temperatures. We then take concentrations as abscissæ, and values of *f/f′* as ordinates, and draw curves, from which the following table is constructed :—

TABLE II.

c.	*f/f′.*			*f/f′* (mean).
	21°.	18°.	15°.	
0·5	1·017	1·017	1·017	1·017
1·0	1·038	1·033	1·036	1·036
2·0	1·073	1·067	1·075	1·072
3·0	1·119	1·110	1·122	1·117
4·0	1·183	1·180	1·179	1·181
5·0	1·250	1·247	1·245	1·247
6·0	1·310	1·310	—	1·310

In Table III these results are compared with those obtained by other observers.

Dieterici's numbers (*Ann. Phys. Chem.*, 1891, **42**, 513) were obtained at 0° by a method depending on the use of a Bunsen calorimeter. Tammann's numbers were obtained at 100°; they are quoted here from Dieterici's paper. Emden's numbers (*Ann. Phys. Chem.*, 1887, **31**, 145) were the means of values obtained between about 18° and 95°. The numbers in the table, we obtained from his results by graphical interpolation.

TABLE III.

c.	f/f'.			T. Ewan and Ormandy.
	Dieterici	Tammann.	Emden.	
0·5	—	—	—	1·017
1·0	1·036	1·033	1·039	1·036
2·0	1·074	1·073	1·080	1·072
3·0	1·120	1·118	1·127	1·117
4·0	1·176	1·171	1·187	1·181
5·0	1·241	1·232	1·252	1·247
6·0	1·315	1·302	—	1·310

We have also made a set of measurements of the vapour pressures of solutions of cupric chloride. The solutions were made up in the way described in the beginning of this paper, from water and crystallised cupric chloride, $CuCl_2,2H_2O$. An analysis of the material used gave the following numbers:—

	Found.	Calculated for $CuCl_2,2H_2O$.
Cu	37·28	37·32

The salt was prepared by recrystallising copper chloride, bought as pure, from dilute hydrochloric acid, and drying the crystals in an air-bath at 45—50°.

The following table contains the numbers obtained. In it

s = concentration of the solutions in grams $CuCl_2$ in 1 gram water.
t = temperature of the solution.
t' = dew point.
f = vapour pressure of pure water at t.
f' = " " solution "

TABLE IV.—*Copper Chloride.*

s.	*t*.	*t′*.	*f*.	*f′*.	*f*/*f′*.	No. of readings of dew point.	Greatest difference between two readings.
0·0169	21·023	20·924	18·521	18·410	1·006	3	0·01°
0·0323	21·010	20·810	18·506	18·282	1·012	2	0·01
0·0560	21·005	20·640	18·501	18·092	1·023	2	0·01
0·0805	20·967	20·322	18·458	17·741	1·040	3	0·02
0·1299	20·920	20·074	18·405	17·472	1·053	3	0·03
0·2018	20·930	19·507	18·417	16·868	1·092	4	0·07
0·2480	20·900	19·001	18·383	16·347	1·125	2	0·02
0·2945	21·040	18·817	18·522	16·162	1·146	3	0·04
0·4398	20·970	17·567	18·462	14·946	1·235	2	0·01
0·0207	18·000	17·855	15·357	15·219	1·009	3	0·01°
0·0373	17·950	17·685	15·309	15·058	1·017	2	0·01
0·0736	17·930	17·457	15·290	14·842	1·030	2	0·01
0·1069	17·950	17·218	15·309	14·621	1·047	3	0·01
0·1467	17·983	16·981	15·341	14·404	1·065	3	0·00
0·1798	18·198	16·905	15·550	14·335	1 085	4	0·02
0·3267	18·190	15·712	15·542	13·291	1·169	2	0·00
0·4437	18·190	14·715	15·542	12·470	1·246	4	0·03
0·0207	15·770	15·611	13·341	13·206	1·010	3	0·02
0 0503	15·797	15·463	13·364	13·081	1·022	3	0·03
0·1099	15·920	15·194	13·468	12·859	1·047	5	0·04
0·1631	15·983	14·844	13·522	12·574	1·075	3	0·02
0·2487	16·060	14·266	13·588	12·115	1·122	3	0·02
0·3198	16·032	13·655	13·564	11·647	1·165	4	0·05
0·4099	16·097	13·009	13·620	11·168	1·219	3	0·00
0·5108	16·310	12 117	13·806	10·538	1·310	4	0 14
0·2182	14·425	12·884	12·239	11·078	1·105	4	0·02
0·3147	14·222	11·952	12·080	10·425	1·159	4	0·01
0·3984	14 267	11·223	12·114	9·938	1·219	3	0·02
0·6698	14·808	9·769	12·542	9·028	1·389	5	0·07
0·7489	14·354	8·360	12·184	8·197	1·486	5	0 05

We have attempted using these numbers to calculate the heats of dilution of some solutions of copper chloride by means of the well known formula of Kirchhoff (*Ann. Phys. Chem.*, 1858, **103**, 177), or *Gesammelte Abhandlungen*, 454). This may be written

$$\frac{\partial Q}{\partial m} = -\frac{R\theta^2}{J}\left[\frac{d}{d\theta}\log f - \frac{\partial}{\partial\theta}\log f'\right],$$

where heat given out by the system is considered positive. $\frac{\partial Q}{\partial m}$

may be regarded as the heat evolved on adding 1 gram of water to an infinite quantity of the solution.

R is the gas constant for aqueous vapour. It is assumed here that saturated steam at ordinary temperatures may be regarded as a perfect gas.

θ is the absolute temperature, and J the mechanical equivalent of heat. f and f' are the vapour pressures of water and solution respectively.

$\frac{\partial}{\partial\theta}\log f'$ was calculated from the vapour pressure determinations briefly as follows:—

The values of f', contained in Table IV, were obtained at temperatures differing slightly from 21°, 18°, 16°, and 14·5° respectively. The numbers corresponding exactly to these temperatures were calculated by assuming that f/f' is constant through the small range of temperature separating the point at which the determination actually took place from that for which the value of f' was required. As this range was generally about 0·1°, the error committed by making this assumption is negligible. From the numbers thus obtained we interpolated the values of f' at the four temperatures above mentioned, for solutions containing 0·05, 0·1, and 0·2 gram $CuCl_2$ in 1 gram of water. For this interpolation we used the following formulæ, in which s is the concentration in grams of $CuCl_2$ in 1 gram water, and $(f - f')$ is the difference between vapour pressure of water and that of the solution:—

$$\left.\begin{aligned} (f - f')_{21^\circ} &= 7{\cdot}6314\,s + 1{\cdot}1111\,s^2 \\ (f - f')_{18^\circ} &= 6{\cdot}4075\,s + 1{\cdot}015\,s^2 \\ (f - f')_{16^\circ} &= 5{\cdot}3624\,s + 1{\cdot}8586\,s^2 \\ (f - f')_{14\cdot5^\circ} &= 5{\cdot}1525\,s + 0{\cdot}6396\,s^2 - 0{\cdot}46418\,s^3 \end{aligned}\right\} \ldots \quad (A).$$

We now expressed the numbers thus obtained by means of formulæ of the form given by Magnus, viz.:—

$$f' = a\,.\,10^{\frac{bt}{c+t}} \ldots\ldots\ldots\ldots\ldots\ldots \quad (B.)$$

where a, b, and c are constants.

By differentiating the expression B with respect to t, we get:—

$$\frac{\partial}{\partial t}\log f' \left(= \frac{\partial}{\partial\theta}\log f'\right) = \frac{bc\log_e 10}{(c + t)^2}.$$

In order to be able to calculate more accurately the constants of the formula B than was possible by means of the numbers obtained over the small range of temperature through which we were able to use our apparatus, we also made use of the vapour pressures of the solutions at their freezing points. The vapour pressure of an aqueous solution is at its freezing point the same as that of ice at the same temperature. The freezing points of the solutions were obtained from a set of measurements made by one of us, which are not yet published. The vapour pressures of ice were taken from the table calculated by Ramsay and Young (*Phil. Trans.*, 1884, ii, 476); a small correction (0·001—2 mm.) was applied to them, owing to the fact that Ramsay and Young's calculation was based on Regnault's formula E, whilst we used his formula D. The following are the numbers used:—

TABLE V.

s.	Freezing point.	f.	f'.
0·05	−1·905	4·010	3·935
0·1	−4·12	3·411	3·258
0·2	−9·63	2·253	1·957

The constants in formula B, which were used, are the following:—

TABLE VI.

s.	a.	b.	c.
0·05	4·5116	8·4049	271·4
0·1	4·3978	8·1790	262·77
0·2	4·1171	6·9722	217·5

It may be pointed out that the constant a in the preceding table represents the vapour pressure of the solution at 0°.

The tables which follow contain the numerical results of the calculations. In Table VII t = temperature of the solution, f' = its vapour pressure, $(f - f')$ = diminution of the vapour pressure, $(f - f')$ calc. is the diminution calculated by means of the formulæ A. The difference between the calculated numbers and those found experimentally only in one case exceeds 0·1 mm. The algebraic sum of the differences is approximately zero, so that the formulæ may be taken as fairly representing the results.

TABLE VII.

$t = 21°$.

s.	f'.	$(f - f')$.	$(f - f')$ calc.	Diff.
0·0169	18·384	0·111	0·129	+0·018
0·0322	18·271	0·224	0·247	+0·023
0·0560	18·077	0·418	0·431	+0·013
0·0805	17·776	0·719	0·621	−0·098
0·1299	17·557	0·938	1·010	+0·072
0·2018	16·939	1·556	1·585	+0·029
0·2480	16·446	2·049	1·960	−0·089
0·2945	16·138	2·357	2·344	−0·013
0·4399	14·973	3·522	3·572	+0·050
			Sum........	+0·205 −0·200

$t = 18°$.

s.	f'.	$(f - f')$.	$(f - f')$ calc.	Diff.
0·0207	15·219	0·138	0·133	−0·005
0·0373	15·109	0·248	0·241	−0·007
0·0736	14·907	0·450	0·477	+0·027
0·1068	14·667	0·690	0·686	−0·004
0·1467	14·419	0·938	0·962	+0·024
0·1798	14·157	1·200	1·185	−0·015
0·3267	13·133	2·224	2·202	−0·022
0·4437	12·322	3·035	3·043	+0·008
			Sum........	+0·059 −0·053

$t = 16°$.

s.	f'.	$(f - f')$.	$(f - f')$ calc.	Diff.
0·02 7	13·399	0·137	0·111	−0·026
0·0503	13·249	0·287	0·274	−0·013
0·1099	12·924	0·612	0·612	0·000
0·1631	12·587	0·949	0·924	−0·025
0·2487	12·068	1·468	1·449	−0·019
0·3198	11·623	1·913	1·905	−0·008
0·4099	11·098	2·438	2·510	+0·072
0·5108	10·332	3·204	3·224	+0·020
			Sum........	+0·092 −0·091

TABLE VII—*continued.*

$t = 14·5°$.				
s.	f'.	$(f - f')$.	$(f - f')$ calc.	Diff.
0·2182	11·131	1·167	1·150	−0·017
0·3147	10·613	1·685	1·671	−0·014
0·3984	10 089	2·209	2·125	−0·084
0·6695	8·852	3·446	3·597	+0 151
0·7489	8·274	4·024	4·023	−0·001
			Sum........	+0·151 −0·116

Table VIII contains under f' the vapour pressures (interpolated from the formulæ A) of solutions containing 0·05, 0·1, and 0·2 gram of $CuCl_2$ in 1 gram water, under "f' calc." the values calculated from the formulæ B. The agreements between the two sets of numbers is very close indeed.

TABLE VIII.

$s = 0·05$.				$s = 0·1$.			
t.	f'.	f' calc.	Diff.	t.	f'.	f' calc.	Diff.
21°	18·111	18·112	+0·001	21°	17·721	17·721	0·000
18	15·033	15·035	+0·002	18	14·706	14·668	−0 038
16	13·263	13·251	−0·012	16	12·981	12·962	−0 019
14·5°	12·039	12 040	+0·001	14·5°	11·776	11·776	0·000
−1·905°	3·935	3·935	0·000	−4·12°	3·258	3·258	0·000

$s = 0·2$.			
t.	f'.	f' calc.	Diff.
21°	16·924	16·924	0·000
18	14·035	14·044	+0·009
16	12·389	12·370	−0·019
14·5°	11·243	11·229	−0·014
−9·63°	1·957	1·957	0·000

Table IX contains the values of $\frac{\partial Q}{\partial m}$ calculated from Kirchhoff's formula and those obtained from J. Thomsen's numbers.

In Kirchhoff's formula we have

$$J = 42355 \text{ grm. cm.}$$

$$R = 4709{\cdot}5 \frac{\text{grm. cm.}}{{}^\circ\text{C.}}.$$

$\theta = 291$ (Thomsen's experiments were made about 18° C.).

$\frac{d}{d\theta} \log f$ (at 18°) calculated from Regnault's formula D is 0·062653.

TABLE IX.

s.	m_s.	$\frac{\partial}{\partial\theta} \log f/f'$.	$\frac{\partial Q}{\partial m}$ (E. and O.).	$\frac{\partial Q}{\partial m}$ (Thomsen).	Diff.
0·05	2508	−0·000065	0·61	0·22	0·39
0·1	1164	−0·000129	1·21	0·78	0·43
0·2	492	−0·000313	2·94	2·48	0·46

The numbers in the column $\frac{\partial Q}{\partial m}$ (Thomsen) have been obtained as follows: Thomsen (*Thermochem. Unters.*, 3, 113) gives the numbers contained in Table X under Q as the amounts of heat evolved on adding m grams of water to a solution containing 1 gram. mol. $CuCl_2$ in 180 grams of water. The numbers under Q calc. are obtained from the formula given by Thomsen (*loc. cit.*, p. 24).

$$Q = \frac{m}{m + 369{\cdot}5} \times 4976{\cdot}3;$$

differentiating this we get:—

$$\frac{\partial Q}{\partial m} = \frac{1838900}{(m + 369{\cdot}5)^2},$$

from which the values of $\frac{\partial Q}{\partial m}$ (Thomsen) are calculated by means of the numbers under m_s in Table IX.

TABLE X.

m.	Q.	Q calc.	Diff.
180	1630	1630	±0
360	2458	2456	−2
720	3336	3289	+47
1620	4052	4052	±0
3420	4510	4491	−19

Although Thomsen's experimental values of $\frac{\partial Q}{\partial m}$ in Table IX do not agree very well with those calculated from our observations, it is easy to see that very small errors in the determinations of the vapour pressures are capable of accounting for the differences, by adopting the plan originally used by Kirchhoff (*Pogg. Ann.*, **104**, 612, 1858) of calculating the vapour pressures from the heats of dilution. He transformed the expression already given into the form—

$$\log f/f' = c + \frac{J}{R \,.\, \log_e 10} \, \frac{1}{\theta} \, \frac{\partial Q}{\partial m} \quad \dots\dots\dots\dots \quad (C).$$

The logarithm is taken to the base 10. c is a constant, and is calculated by means of any one determination of the vapour pressure of the solution. Using the vapour pressures found at 21° in Table III we find the values of c:—

s.	*c.*
0·05	0·006162
0·1	0·008180
0·2	0·005635

In Table XI the numbers calculated from equation C by means of these constants are compared with the experimental numbers from Table VIII.

TABLE XI.

s = 0·05.				*s* = 0·1.			
t.	*f′* calc.	*f′* found.	Diff.	*t.*	*f′* calc.	*f′* found.	Diff.
−1·905	3·925	3·935	+0·010	−4·12	3·261	3·258	−0·003
14·5	12·041	12·039	−0·002	14·5	11·777	11·776	−0·001
16·0	13·253	13·263	+0·010	16·0	12·964	12·981	+0·017
18·0	15·037	15·033	−0·004	18·0	14·711	14·706	−0·005

s = 0·2.

t.	*f′* calc.	*f′* found.	Diff.
−9·63	2·044	1·957	−0·087
14·5	11·208	11·243	+0·035
16·0	12·370	12·389	+0·019
18·0	14·042	14·035	−0·007

The agreement is on the whole satisfactory.

LXX.—*The Hydrazines of Quinoline.*

By S. F. Dufton, B.A., D.Sc., Head Science Master of the Bradford Grammar School.

I have continued the work described in my last paper (Trans., 1891, **59**, 756), and having found a new and convenient method of nitrating quinoline, giving large quantities of ananitroquinoline (called meta- in the former paper in accordance with the old nomenclature), have worked out the preparation and properties of the anahydrazine and some of its derivatives. All the compounds of this series are remarkable for stability and beauty of form, the hydrazine itself having a high melting point and crystallising from hot water. Incidentally I have also discovered the "picric acid" of the quinoline series, dinitrohydroxyquinoline, a yellow dye of great beauty.

Part II.—The Nitration of Quinoline.

The necessity which arose, in the course of my work, of preparing nitroquinoline on a comparatively large scale soon rendered evident the extreme inconvenience of the methods already described, and led me to spend considerable time in trying to find the conditions under which the nitration would take place most readily.

In the old method usually employed, due to Claus and Kramer (*Ber.*, **18**, 1245), quinoline is heated at 80° for 10 hours with a mixture of equal volumes of fuming nitric and strong sulphuric acids, after first dissolving the quinoline in ordinary nitric acid. The disadvantages of this are the formation of dinitroquinolines, and, what is more troublesome, the very large excess of acid which has to be employed; the latter, when diluted so as to prevent, upon neutralisation by soda, the crystallisation of sodium sulphate with the precipitated nitroquinolines, renders the bulk of liquid to be operated on very unwieldy.

The method described by Nölting and Trautmann (*Ber.*, **23**, 3654), of dissolving quinoline in strong sulphuric acid and adding the calculated quantity of fuming nitric acid with, at the same time, Nordhausen sulphuric acid containing sufficient anhydride to combine with all the water produced in the action, was found to be of no practical value. Although no dinitroquinolines are produced, the nitration is extremely slow even at 100°, whilst the very large excess of sulphuric acid used makes the subsequent treatment of the liquid even more troublesome than in the other process.

On this account, I was led to try if the dehydration of quinoline nitrate, with formation of nitroquinoline, could not be more readily effected than the nitration of quinoline sulphate, as in Nölting and Trautmann's method, and found, indeed, that whereas the latter operation requires at least a week, even on the water-bath, the former may be completed in the cold in less than an hour. The method found ultimately to give the best results was:—

To 50 grams of quinoline, in a glass evaporating basin floating in a dish of cold water, is added gradually from a burette slightly more than the calculated volume of fuming nitric acid (sp. gr. 1·5). When cold, the solid cake of nitrate is roughly powdered and added in about five portions to 50 c.c. of strong sulphuric acid contained in a litre flask, adding 10 c.c. of fuming sulphuric acid (sp. gr. 2·0) after each addition of nitrate, and keeping the mixture cool. The completion of nitration, which takes from half an hour to an hour, is recognised by diluting a few drops of the mixture with water and neutralising with caustic soda; the smell of quinoline will have practically disappeared, and the milky precipitate produced by the soda solidifies after a few minutes to a mass of crystals. The mixture is then poured into water, filtered, after cooling, from a small quantity of a yellow, crystalline substance, and gradually neutralised with caustic soda. When cold, the crude nitroquinolines precipitated are collected and dissolved in a large quantity of boiling, very dilute nitric acid; on cooling, the nitrate of ananitroquinoline crystallises out in powdery crystals which are almost insoluble in cold water, and very different from the easily soluble, large, well-formed tablets of the ortho-compound.

The mother liquors from the ananitrate are treated with excess of caustic soda, and the precipitate, after being well pressed, is crystallised from alcohol; one crystallisation gives practically pure orthonitroquinoline. The alcoholic mother liquor contains both ortho- and ana-compounds, the latter of which is extremely soluble in alcohol; after distilling off the solvent, these are worked up with the next lot of nitrates.

The recrystallised ananitrate is heated in a dish with a small quantity of water, and strong caustic soda added until the liquid, after continued boiling, remains slightly alkaline; the nitroquinoline thus liberated is collected, washed with water, dried by gently heating in a dish over a small flame, and crystallised from light petroleum (b. p. 100°), when it forms pure, almost white needles melting at 72°.

The yield of nitroquinolines is practically quantitative; in one operation, from 300 grams of quinoline, 200 grams of ananitroquinoline and 150 grams of orthonitroquinoline were obtained in a pure state, a yield of 87 per cent. of the theoretical amount.

The quantity of the insoluble yellow substance mentioned above is about 3 per cent. of the quinoline taken. It explodes on heating, and has both acid and basic properties, being, as Armstrong has suggested, a phenol; it is, in fact, dinitrohydroxyquinoline, the "picric acid" of the quinoline series. When recrystallised from a large quantity of boiling water, in which it is sparingly soluble, it forms small, shining leaflets of a greenish-yellow colour, which decompose entirely at about 255°.

The analytical results were:—

0·2545 gram of substance gave 0·4302 gram CO_2 and 0·0592 gram H_2O.

0·1622 gram of substance gave 23·8 c.c. N at 13° and 771 mm.

	Theory for $C_9H_4N(NO_2)_2 \cdot OH$.	Found.	
		I.	II.
C............	46·0	46·1	—
H............	2·1	2·2	—
N............	17·9	—	17·8

The compound possesses great tinctorial power and dyes wool, best in slightly ammonial aqueous solution, a beautiful, pure yellow, almost indistinguishable from that of picric acid.

The two nitroquinolines and the yellow dye, described above, seem to be the only products of the nitration. Some alcoholic mother liquors once deposited plates melting at 54° (all the four known nitroquinolines crystallise in needles), but they were found to consist of ortho- and ana-nitroquinoline crystallised together, for on treatment with nitric acid they were easily separated as nitrates. The nitroquinolines were then liberated by soda, and after recrystallising from light petroleum, identified by their melting points. It was further shown that by simply mixing about equal proportions of the ortho- and ana-nitro-compounds (m. p. 89° and 72° respectively) the melting point of the mixture was reduced to 53—54°.

PART III.—ANAQUINOLINEHYDRAZINE.

With a convenient method of obtaining ananitroquinoline on a large scale, the preparation of the corresponding hydrazine upon the lines followed in the case of the ortho-compound was found to present no difficulty. The compounds obtained differ to a considerable extent from those of the ortho-series in appearance and solubility. One remarkable feature common to both is the intense red colour of the monacid salts of the amine and hydrazine.

Anamidoquinoline.

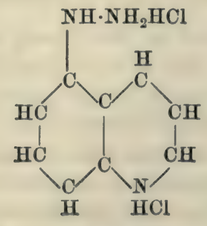
Ananitroquinoline is reduced by mixing it with the calculated quantity of stannous chloride, both in hydrochloric acid solution. After the nearly solid mixture has become quite cold, caustic soda is gradually added until in excess, and the liquid extracted four times with ether. The ethereal extract, after distilling off most of the solvent, is allowed to crystallise, when the greater part of the amido-compound is obtained in yellow crystals, practically pure. The later portions from the mother liquor are darker, and may be best purified by crystallisation from hot water.

Unlike the ortho-compound, anamidoquinoline cannot be distilled even under diminished pressure without considerable loss; but, being less oxidisable than the ortho-compound, it is obtained pure in the way above described without any difficulty.

Anaquinolinehydrazine.

The amido-compound is treated with hydrochloric acid, and the hydrochloride carefully ground in a mortar to an impalpable powder. It is then mixed with a considerable excess of hydrochloric acid, and, after cooling, diazotised in the ordinary way. The solution, after being filtered rapidly through a hardened filter paper on a Büchner porcelain funnel to separate the common salt which has crystallised out, is put once more in the freezing mixture, and the calculated quantity of stannous chloride, dissolved in hydrochloric acid, added. The stannochloride of the hydrazine, at once thrown down, is collected, heated with much water in a large dish, and a current of sulphuretted hydrogen passed through until all the tin is precipitated. After filtering and concentrating the solution, the dihydrochloride of the hydrazine separates out in the form of beautiful, lemon-yellow needles which turn brown at 225° and melt at 248°.

Analysis confirms the formula



	Calculated.	Found.
Cl................	30·6	30·6

On treating the aqueous solution with caustic soda, first a deep blood-red colour is produced, indicating the formation of the monohydrochloride, and then, with excess of alkali, a greenish-white, crystalline precipitate of the hydrazine is thrown down. Recrystallised from water, the substance forms beautiful, yellow needles which, after drying at 100°, melt at 150—151°. The aqueous solution of the hydrazine reduces Fehling's solution slowly in the cold, but rapidly when heated, with evolution of nitrogen, and production of a strong odour like that of quinoline.

The hydrazine is insoluble in light petroleum, sparingly soluble in benzene, more so in ether, and readily in alcohol.

Upon analysis—

0·1298 gram of substance gave 28·5 c.c. N at 17° and 773 mm.

	Calculated for $C_9H_6N{\cdot}NH{\cdot}NH_2$.	Found.
N	26·4	26·3

Anaquinolinesemicarbazide.

On adding potassium cyanate to a solution of the hydrazine hydrochloride in water, a yellow precipitate is thrown down, which becomes nearly white on heating. This substance, the semicarbazide, crystallises from water in needles, and in small, hard prisms from alcohol, in both cases being slightly brownish. The compound softens at 185°, and decomposes entirely at 255°. Crystallised from alcohol and dried in a vacuum, it still contains 1 mol. H_2O, which is driven off very slowly even at 100°.

0·1084 gram of substance gave 23·2 c.c. N at 20° and 772 mm.

	Calculated for $C_9H_6N{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2 + H_2O$.	Found.
N	25·4	25·4

The Pyruvic Acid Hydrazone.

On adding pyruvic acid to the strong aqueous solution of the hydrazine hydrochloride, the mixture becomes almost solid from the separation of the hydrochloride of the pyruvic acid hydrazone. This substance may be recrystallised from water, and melts at 193°. On the addition of sodium acetate to the strong aqueous solution of the salt, the hydrazone is liberated as a beautiful, bright-red crystalline precipitate, differing from the corresponding ortho-compound by being soluble in water and by its vivid colour; this, however, changes to yellow, on drying, with loss of water of crystallisation; the substance melts at 185°.

For analysis, it was crystallised from alcohol, and dried at 100°:—

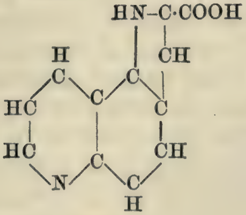
0·15 gram of substance gave 23·2 c.c. N at 17° and 767 mm.

	Calculated for $C_9H_6N\cdot NH\cdot N{:}C(CH_3)\cdot COOH$.	Found.
N	18·3	18·3

Anaquinindole-α-carboxylic Acid.

As in the case of the ortho-compound, the indole condensation takes place with remarkable ease when the pyruvic acid hydrazone is simply boiled for about an hour with strong hydrochloric acid. The liquid darkens and becomes filled with yellow crystals, which are the hydrochloride of the indole acid. This salt may be recrystallised from a small quantity of water, but much water precipitates the acid, which is almost insoluble in water and alcohol. It may easily be crystallised, however, by making use of the ready dissociation of its ammonium salt by heat. The acid is dissolved in water with addition of a few drops of ammonia, and allowed to evaporate in a beaker on the water-bath; as the ammonia is driven off, the acid crystallises out in beautiful, yellow needles which decompose at about 300°.

The formula of the compound,



,

was confirmed by the following analysis:—

0·1715 gram of substance gave 19·4 c.c. N at 21° and 761 mm.

	Calculated for $C_{12}H_8N_2O_2$.	Found.
N	13·2	13·2

The Acetone Hydrazone.

On mixing the hydrazine and acetone, a dark syrup forms with evolution of heat; this crystallises completely on cooling, and is then powdered and washed with cold alcohol. When recrystallised from hot alcohol, it forms large, lustrous, yellowish-brown prisms which melt at 138—140°.

0·14 gram of substance gave 25·4 c.c. N at 21° and 762 mm.

	Calculated for $C_9H_6N\cdot NH\cdot N{:}C(CH_3)_2$.	Found.
N	21·1	21·3

The Benzaldehyde Hydrazone.

On mixing the hydrazine with benzaldehyde, great heat is evolved, and a solid, crystalline mass obtained; this is purified in the same way as the acetone compound, and recrystallised from boiling alcohol; it forms lustrous, brown, cube-like crystals which melt at 194°.

0·1502 gram of substance gave 21·17 c.c. N at 19° and 763 mm.

	Calculated for $C_9H_6N\cdot NH\cdot N{:}CH\cdot C_6H_5$.	Found.
N	17·0	17·0

Anaquinolinemethylpyrazolone.

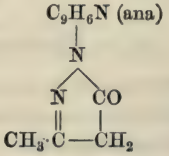
On mixing the hydrazine and ethyl acetoacetate in molecular proportion, a dark syrup is formed with slight evolution of heat. The mixture is placed in the steam oven, and, after several hours, crystallisation sets in, and a solid mass results; this is finely powdered, and washed with cold anhydrous acetone, which removes the greater portion of the coloured products leaving a light-brown powder. This, the pyrazolone, is then purified by repeated crystallisation from water, using animal charcoal, when it becomes white. The substance is almost as soluble in cold water as in hot, and must therefore be crystallised by evaporation in a vacuum or on the water-bath. It is exceedingly soluble in alcohol, but does not crystallise from it. The pure substance melts, without decomposition, at 186°.

On analysis:—

0·1412 gram of substance gave 22·3 c.c. N at 19° and 753 mm.

	Calculated.	Found.
N	18·66	18·5

which confirms the formula



Cambridge University Laboratory.

LXXI.—*The Origin of Colour. Note on the Appearance of Colour in Quinoline Derivatives and of Fluorescence in Quinine Salts.*

By Henry E. Armstrong.

Several of the quinoline derivatives described by Dr. Dufton in his two papers (Trans., 1891, 756; 1892, p. 782) exhibit noteworthy peculiarities which I venture to think merit examination from the point of view advocated by me in recent years in discussing the relation of colour to constitution ("The origin of colour," Proc., 1888, 27; 1892, 101); on seeing Dr. Dufton's preparations, I was fairly startled by the vividness of the colour which several possessed, the bright red of the acid salts of the amine and hydrazine being especially remarkable.

The nitroquinolines display a faintly yellow colour, but it is probable that this is conditioned by the presence of traces of the hydroxy-derivative or quinolinol,[*] the discovery of which among the nitration products of quinoline is of interest, as it affords further evidence that the production of nitro-substitution derivatives is preceded by that of addition compounds (compare Proc., 1891, 89).

The ortho-derivatives described by Dr. Dufton, excepting the pyruvic hydrazone,[†] apparently are colourless substances; the ana-derivatives, however, are mostly coloured; it could scarcely have been predicted that such compounds would manifest colour, and in consequence it appears necessary to reconsider their structure. I have no hesitation in asserting that they must be *quinonoid* compounds.

It is a noteworthy circumstance that quinonoid formulæ cannot be assigned to the ortho-compounds, which, in point of fact, are colourless, it being impossible to dispose of the affinities except in the conventional manner; but this is not the case with the ana-derivatives: the ana-amide, for example, may be represented thus :—

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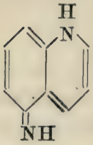
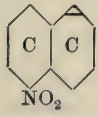
[*] *-inol* appears to be an appropriate systematic termination for *-ols* derived from azotised basic cycloids; the prefixes *homo-* and *hetero-* might be used to indicate the presence of the hydroxyl either in the same nucleus with the nitrogen or in that remote from it. Dr. Dufton's compound is doubtless a dinitroheteroquinolinol.

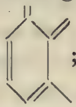
[†] Many hydrazones are described as coloured, but it is not certain that they are as a class: being very sensitive and easily altered by exposure to light and air, it is probable that the colour is due in some, if not in all, cases to the presence of impurity.

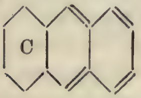


Ana-" amido-"quinoline.



Ananitroquinoline.*

It is here assumed that the "centric" (C) structure of quinoline is preserved in the case of the nitro-compound, while the "ethenoid" structure of an orthoquinone is assumed by the ana-amine in consequence of the transference of an hydrogen atom, and that the latter is in reality (in the form of acid salt) an *imido-* and not an amido-compound. Looked at in the manner advocated by Bamberger, the "amine" is the equivalent of a tri-derivative of the type  ; *i.e.*, it is a mono-derivative of a compound of the orthoquinone type. From this point of view, the appearance of colour in the ana-derivatives of quinoline, being conditioned by isodynamic change (Proc., 1892, 203), is evidence of considerable intramolecular mobility.

Finally, I wish to point out that it may eventually prove to be possible to explain the fluorescence of certain salts of quinine by the application of a similar principle. In my first communication on the origin of colour, I said that anthracene was "significantly fluorescent," having the idea before me that fluorescence might be regarded as "the beginning of colour," and further study of the question has served to confirm this opinion; anthracene, if represented as unsymmetrical (compare Proc., 1890, 102), a view which its entire behaviour justifies and indeed enforces, is a compound of the orthoquinone type, , and it is significant that fluorene, which cannot be so represented, has proved to be non-fluorescent (Hodgkinson and Matthews, Trans., 1883, **43**, 163).

It is well known that the oxy-salts of quinine are alone fluorescent, salts like the chlorhydride not being so; it is conceivable that this is due to the inferior stability of the former in solution, and that owing to the occurrence of dissociation, a condition is engendered favouring the passage by isodynamic change from the non-fluorescent centric to the fluorescent ethenoid condition, such as it has been above suggested takes place in the case of ana-derivatives of quinoline.

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* The formula here used is that suggested by me in 1887 (compare *Journ. Soc. Chem. Ind.*, 486), a line being drawn across the angle instead of printing in the N symbol.

LXXII.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. XXV.—*Dicarboxyglutaconic Acid.*

By S. Ruhemann, Ph.D., M.A., and R. S. Morrell, B.A.

The study of the ethereal salt of this acid was undertaken with the view of ascertaining whether the action of ammonia caused condensation, with the formation of a derivative of pyridine, as in the case of citric and aconitic acids. Though, as previously shown (Trans., 1891, **59**, 743), such a change really does occur, giving rise to the diamide of dihydroxydinicotinic acid, only a small portion of the ethereal salt undergoes this transformation under the conditions of our experiments, the larger part splitting up into malonamide and the ethylic salt of amidoethylenedicarboxylic acid, according to the equation

$$(COOC_2H_5)_2CH\cdot CH{:}C(COOC_2H_5)_2 + 3NH_3 = CH_2(CONH_2)_2 + 2C_2H_5\cdot OH + NH_2\cdot CH{:}C(COOC_2H_5)_2.$$

An analogous action takes place with the derivatives of the ethereal salt of dicarboxyglutaconic acid. The benzyl derivative, when acted on by strong ammonia, yields, besides benzylmalonamide, the same substance, namely, the ethereal salt of amidoethylenedicarboxylic acid. To the analysis of this compound, published in our previous paper, we can now add the determination of its molecular weight by Raoult's method, using benzene as the solvent.

Weight of substance	0·3372 gram
,, benzene	22·4990 grams
Melting point of benzene	4·98°
,, the mixture	4·60°
Depression of the melting point	0·38°
Molecular weight derived from the above data	190
Theory for $C_8H_{13}NO_4$	187

The action of ammonia on the ethyl salt of dicarboxyglutaconic acid does not seem to go so far as to bring about the formation of the diamide of amidoethylenedicarboxylic acid. Even on allowing the ethyl salt to remain in contact with strong aqueous ammonia for a long time, the action proceeds for the most part according to the above equation. However, in the course of several months, there is produced, besides the ethereal salt of amidoethylenedicarboxylic acid, a small quantity of the monamido-compound, having the formula $CH(NH_2)\colon C(CO\cdot NH_2)\cdot COOC_2H_5$.

This substance is easily isolated: the solid which separates from the ammoniacal solution, after the removal of most of the ammonia by a current of air, is shaken with ether, which dissolves the ethyl salt of amidoethylenedicarboxylic acid, leaving the monamide. On recrystallisation from hot water, it separates in colourless plates melting at 169—170°; it gave numbers corresponding with the formula $CH(NH_2)\colon C(CO\cdot NH_2)\cdot COOC_2H_5$.

I. 0·1905 gram of substance gave 0·1140 gram H_2O and 0·3150 gram CO_2.

II. 0·1702 gram of substance gave 0·1015 gram H_2O and 0 2835 gram CO_2.

III. 0·1085 gram of substance gave 16 6 c.c. moist nitrogen at 20° and 763 mm.

	Theory for $C_6H_{10}N_2O_3$.	Found.		
		I.	II.	III.
C	45·56	45·10	45·40	—
H	6·33	6·65	6·63	—
N	17·72	—	—	17·56

An attempt to displace the other ethoxy-group of the ethyl salt of amidoethylenedicarboxylic acid by an amido-group was unsuccessful. On heating the diethyl salt with strong aqueous ammonia, in a closed tube at 100°, it is decomposed, most probably in the manner indicated by the following equation:—

$$CH(NH_2)\colon C(COOC_2H_5)_2 + 2NH_3 + H_2O = HCONH_2 + CH_2(CO\cdot NH_2)_2.$$

The contents of the tube, when evaporated on the water-bath, left a white, crystalline substance which, after recrystallisation from water, melted at 169—170°.

This was identified as malonamide by its behaviour and by a nitrogen determination.

0·0995 gram of substance gave 23·8 c.c. moist nitrogen measured at 19° and 757 mm.

	Theory for $C_3H_6N_2O_3$.	Found.
N	27·45	27·38

The splitting up of ethyl amidoethylenedicarboxylate, which takes place under the influence of boiling aqueous ammonia, also occurs when it is heated with baryta water. The study of this reaction was undertaken with the view of isolating the hydroxyethylenedicarboxylic acid. From the barium determination of the former salt we were led to regard it as the barium salt of the hydroxy-acid (*loc. cit.*, p. 748). On further investigation we found, however, that it was a mixture of the barium salts of formic and malonic acids; for, on decomposing it with dilute sulphuric acid and repeatedly shaking the filtrate from the barium sulphate with ether, an organic acid was extracted which crystallised from alcohol in prisms melting at 131°.

The analysis gave numbers corresponding with the formula for malonic acid.

0·1695 gram of substance gave 0·0603 gram H_2O and 0·2145 gram CO_2.

	Theory for $C_3H_4O_4$.	Found.
C	34·61	34·51
H	3·84	3·95

The presence of formic acid was verified by its reactions. The formation of malonic acid from ethyl amidoethylenedicarboxylate indicates that the latter is first transformed into the barium salt of hydroxyethylenedicarboxylic acid, which, however, under the influence of baryta undergoes decomposition in exactly the same way as the hydroxyethylene compounds in general do when boiled with alkalis (see Claisen, *Ber.*, **25**, 1781).

The interesting change which these ethereal salts undergo in contact with strong aqueous ammonia induced us to investigate the action of other organic bases on them, in order to ascertain whether under their influence an analogous change takes place. We have at present completed the study of the action of phenylhydrazine on the above-mentioned compounds, and have found that they are resolved in the same way as when ammonia is used. Both ethereal salts give rise to a derivative of pyrazolone.

Action of Phenylhydrazine on the Ethereal Salts of Dicarboxyglutaconic Acid.

On mixing equal weights of phenylhydrazine and ethyl dicarboxyglutaconate in a flask fitted with a condenser, an action ensues with evolution of heat, and if the mixture is then heated on the water-bath, it gives off ammonia, nitrogen, and benzene. As soon as gas ceases to be evolved, the flask is removed from the water-bath, and, after a short time, colourless needles separate from the dark oil, the separation being accelerated by the addition of ether. The precipitate is washed with ether until the washings are colourless, and the crystals dried in a vacuum over sulphuric acid.

On analysis, the following numbers were obtained:—

I. 0·1615 gram of substance gave 0·0983 gram H_2O and 0·3204 gram CO_2.

II. 0·1638 gram of substance gave 0·1003 gram H_2O and 0·3235 gram CO_2.

III. 0·1638 gram of substance gave 22 c.c. moist nitrogen measured at 21° and 761 mm.

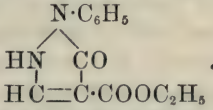
IV. 0·1582 gram of substance gave 22·2 c.c. moist nitrogen measured at 24° and 756 mm.

	Theory for $C_{12}H_{17}N_3O_4$.	Found.			
		I.	II.	III.	IV.
C	53·93	53·45	53·86	—	—
H	6·36	6·74	6·78	—	—
N	15·74	—	—	15·30	15·65

The above analyses indicate that the composition of the product can be represented by the expression $C_{12}H_{17}N_3O_4$. This formula may be interpreted as follows: the ethereal salt of dicarboxyglutaconic acid, when heated with phenylhydrazine, is resolved into the ethyl salts of phenylhydrazilethylenedicarboxylic acid and malonic acid, according to the equation

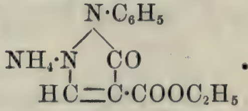
$$CH(COOC_2H_5)_2\cdot CH\colon C(COOC_2H_5)_2 + C_6H_5\cdot NH\cdot NH_2 =$$
$$C_6H_5\cdot NH\cdot NH\cdot CH\colon C(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2.$$

The hydrazine compound then loses alcohol, yielding ethyl phenylpyrazolonemonocarboxylate,



.

This, however, is not the final product, for part of the phenylhydrazine used decomposes into nitrogen, ammonia, and benzene, and the ammonia then combines with the pyrazolone compound, yielding the ammonium salt,



.

This salt, however, rapidly absorbs water, 1 mol. of which is retained even in a vacuum over sulphuric acid. An attempt was made to remove this molecule of water by heating the salt at 100°, but at this temperature it partially dissociates into ammonia and ethyl phenylpyrazolonemonocarboxylate. This decomposition occurs also when it is boiled with water.

The second product of the action between ethyl dicarboxyglutaconate and phenylhydrazine is ethyl malonate. This was isolated from the ethereal solution in the following manner:—The ether was distilled off, and steam passed through the remaining dark-coloured oil; ethyl malonate and phenylhydrazine passed over, leaving a resin. The distillate was then treated with dilute hydrochloric acid and shaken with ether; and the latter, on evaporation, left an oil which boiled at 194°, and on analysis gave numbers agreeing with the formula $CH_2(COOC_2H_5)_2$.

0·1985 gram of substance gave 0·1330 gram H_2O and 0·3803 gram CO_2.

	Theory for. $C_7H_{12}O_4$.	Found.
C	52·50	52·25
H	7·5	7·44

The resolution of ethyl dicarboxglutaconate, under the influence of phenylhydrazine, into the pyrazolone compound and ethyl malonate, which is so readily effected at 100°, also takes place at the ordinary temperature, though very slowly.

Action of Phenylhydrazine on Ethyl Benzyldicarboxyglutaconate.

This action presents a close similarity to that of the hydrazine on ethyl dicarboxyglutaconate, for when phenylhydrazine and ethyl benzyldicarboxyglutaconate are mixed in the proportion of 4·3 grams of the former to 5 grams of the latter no action takes place at first, but on heating to 100° on a water-bath a rapid evolution of gas sets in. As soon as this ceases, the contents of the flask are cooled, and ether added, when a white solid is thrown down, which, from its behaviour and by a nitrogen determination, was shown to be the ammonium salt of ethyl phenylpyrazolonemonocarboxylate.

0·1788 gram of the substance gave 24 c.c. of moist nitrogen measured at 21° and 760 mm.

	Theory for $C_{12}H_{17}N_3O_4$.	Found.
N	15·74	15·30

The ethereal filtrate from this compound was shaken with hydrochloric acid, and the oil obtained on removal of the ether was distilled under diminished pressure. The boiling point was found to be 187° under a pressure of 30 mm.

An analysis showed it to be ethyl benzylmalonate,

$$C_6H_6{\cdot}CH_2{\cdot}CH(COOC_2H_5)_2.$$

0·1930 gram of substance gave 0·1255 gram OH_2 and 0·4742 gram CO_2.

	Theory for $C_{14}H_{18}O_4$.	Found.
C..............	67·20	66·96
H.............	7·20	7·22

Besides the ammonium salt of ethyl phenylpyrazolonemonocarboxylate and ethyl malonate, a small quantity of another substance was found to have been produced by the action of phenylhydrazine on ethyl benzyldicarboxyglutaconate. This is contained in the ethereal filtrate from the pyrazolone derivative, and is precipitated from it by the addition of hydrochloric acid. The compound is insoluble in water, but soluble in alcohol and acetic acid, and crystallises from them in leaflike aggregates of needles. It melts at 258°, and is readily taken up by alkalis.

The very small yield prevented us from fully examining this substance, the amount at our disposal being only sufficient for a nitrogen determination.

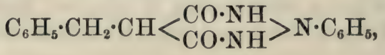
0·1623 gram of substance yielded 21·8 c.c. of moist nitrogen measured at 24° and 757 mm.

This corresponds to 14·97 per cent. of nitrogen.

The compound is no doubt the result of the action of phenylhydrazine on ethyl benzylmalonate, as it is not formed when the hydrazine and ethyl dicarboxyglutaconate are heated together.

The percentage of nitrogen found, 14·97, agrees with that required by the hydrazide of benzylmalonic acid,

$$C_6H_5{\cdot}CH_2{\cdot}CH(CO{\cdot}NH{\cdot}NH{\cdot}C_6H_5)_2,$$

namely, 14·97 per cent., as well as with that of the azimide of benzylmalonic acid,  $C_6H_5{\cdot}CH_2{\cdot}CH{<}\begin{matrix}CO{\cdot}NH\\CO{\cdot}NH\end{matrix}{>}N{\cdot}C_6H_5$, namely, 14·94 per cent.

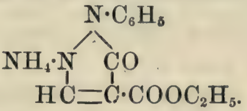
In order to ascertain whether the compound is really the hydrazide, we prepared the latter by heating for a short time a mixture of phenylhydrazine with ethyl benzylmalonate. On the addition of alcohol, colourless crystals were deposited, which, although almost insoluble in alcohol, dissolved in hot glacial acetic acid, and on cooling, separated as colourless needles, very different from the leaflike aggregates of needles of the other substance. The compound, which is the hydrazide of benzylmalonic acid, melts at 242—243°, and is insoluble in alkalis. A nitrogen determination gave the following numbers:—

0·1515 gram of substance yielded 20·2 c.c. of moist nitrogen at 22° and 756 mm.

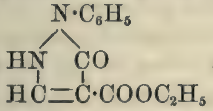
	Theory for $C_{22}H_{22}N_4O_2$.	Found.
N	14·97	15·01

The bye-product of the action of phenylhydrazine on ethyl benzyldicarboxyglutaconate is therefore probably the azimide of benzylmalonic acid.

Phenylpyrazolonemonocarboxylic Acid.

The substance formed from the ethereal salts of dicarboxyglutaconic acid and its benzyl derivative, we regard as the ammonium salt of phenylpyrazolonemonocarboxylic acid, 

This view is supported by the behaviour of the compound. The aqueous solution of the ammonium salt, when treated with dilute hydrochloric acid, is decomposed, colourless crystals being precipitated, which are readily dissolved by ether, leaving ammonium chloride in the aqueous solution. That ammonia is the base combined with the pyrazolone compound was proved by precipitating the platinochloride from the solution by platinic chloride, the analysis giving 43·87 per cent. of platinum.

The pyrazolone compound is slightly soluble in cold water, more readily in boiling water, and on cooling crystallises in needles, which melt not quite sharply at 116°. The substance, dried in a vacuum over sulphuric acid, gave, on analysis, numbers which agree with the formula  .

I. 0·1835 gram of substance gave 0·0920 gram H_2O and 0·4180 gram CO_2.

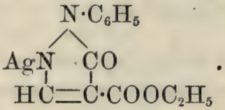
II. 0·1507 gram of substance gave 0·0705 gram H_2O and 0·3172 gram CO_2.

III. 0·1848 gram of substance gave 19·6 c.c. moist nitrogen measured at 18° and 766 mm.

IV. 0·1465 gram of substance gave 15·4 c.c. moist nitrogen measured at 21° and 763 mm.

	Theory for $C_{12}H_{12}N_2O_3$.	Found.			
		I.	II.	III.	IV.
C	62·07	62·12	62·00	—	—
H	5·17	5·57	5·60	—	—
N	12·07	—	—	12·34	12·00

Ethyl phenylpyrazolonemonocarboxylate has acid properties, for it is readily dissolved by ammonia and alkalis. On the addition of silver nitrate to the neutral solution of the ethereal salt in ammonia, it yields a stable silver salt, insoluble in water; it is identical with that thrown down by silver nitrate from the original product of the action of phenylhydrazine on the ethereal salt of the dicarboxyglutaconic acid. Analysis proved the silver salt to have the formula



$$\begin{array}{c} N\cdot C_6H_5 \\ AgN \quad CO \\ HC{=}C\cdot COOC_2H_5 \end{array}$$

.

I. 0·2344 gram of substance gave 0·0730 gram H_2O and 0·3658 gram CO_2.

II. 0·3910 gram of substance left on ignition 0·1242 gram Ag.

III. 0·6250 „ „ „ „ 0·1975 „

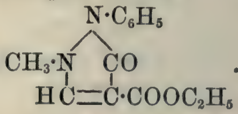
IV. 0 3935 „ „ „ „ 0·1250 „

	Theory for $C_{12}H_{11}Ag_2N_2O_3$.	Found. I.	II.	III.	IV.
C	42·47	42·56	—	—	—
H..........	3·24	3·46	—	—	—
Ag	31·85	—	31·76	31·60	31·75

Ethyl Phenylmethylpyrazolonemonocarboxylate.

This is formed on heating the dry silver salt with methyl iodide on the water-bath in a flask fitted with a reflux condenser. To separate it from the silver iodide, the product is repeatedly extracted with ether, and the ethereal salt evaporated, when an oil is obtained, which soon solidifies to a crystalline mass. This, on recrystallisation from alcohol, yields long, colourless needles melting at 71—72°.

The analytical data agreed with the formula



$$\begin{array}{c} N\cdot C_6H_5 \\ CH_3\cdot N \quad CO \\ HC{=}C\cdot COOC_2H_5 \end{array}$$

.

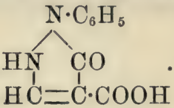
I. 0·1965 gram of substance gave 0·1013 gram H_2O and 0·4569 gram CO_2.

II. 0·1818 gram of substance gave 18 c.c. of moist nitrogen at 20° and 766 mm.

	Theory for $C_{13}H_{14}N_2O_3$.	Found. I.	II.
C	63·41	63·41	—
H	5·69	5·72	—
N...........	11·38	—	11·42

1 : 5 : 4-*Phenylpyrazolonemonocarboxylic Acid.*

The hydrolysis of the ethyl salt, described above, is best effected by boiling it with aqueous potash on a sand-bath in a flask fitted with a reflux condenser. The action is completed after three hours, when the flask is cooled, and dilute hydrochloric acid added to the alkaline solution; the almost colourless precipitate which is thrown down is collected and washed with water until the filtrate remains clear on the addition of silver nitrate. In order to remove any unaltered ethereal salt, the product is washed with ether, in which it is only slightly soluble. For analysis, it was dried in a vacuum over sulphuric acid, and gave results proving the substance to be phenylpyrazolonemonocarboxylic acid,



.

I. 0·1815 gram of substance gave 0·0695 gram H_2O and 0·3907 gram CO_2.

II. 0·1620 gram of substance gave 19·8 c.c. moist nitrogen at 23° and 764 mm.

	Theory for $C_{10}H_8N_2O_3$.	Found. I.	Found. II.
C	58·82	58·70	—
H	3·92	4·25	—
N	13·72	—	13·85

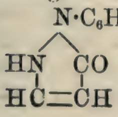
Phenylpyrazolonemonocarboxylic acid is not very stable; it decomposes at 91—92° with evolution of carbon dioxide, and the same decomposition takes place on boiling it with water.

It is very soluble in alcohol and in acetone, is readily soluble in ammonia and alkalis, and the neutral ammoniacal solution on the addition of silver nitrate, yields a slightly coloured silver salt which darkens on warming.

Phenylpyrazolone.

The pyrazolonemonocarboxylic acid, as mentioned above, is readily decomposed by boiling water with the evolution of carbon dioxide. The concentrated aqueous solution, on cooling, deposits prisms, which, on repeated recrystallisation from alcohol, become colourless, and melt at 118°.

A nitrogen determination proved the substance to be phenylpyrazolone,



0·1390 gram of substance yielded 21·6 c.c. of moist nitrogen measured at 22° and 756 mm.

	Theory for $C_9H_8N_2O$.	Found.
N	17·50	17·50

Phenylpyrazolone is very soluble in mineral acids, and also in alkalis, a behaviour which characterises it as a base as well as an acid.

In conclusion we may add that we intend to continue the study of the ethereal salts of dicarboxyglutaconic acid and its derivatives on the lines already indicated in this paper.

LXXIII.—*The Magnetic Rotation of Compounds supposed to Contain Acetyl, or to be of Ketonic Origin.*

By W. H. Perkin, Ph.D., F.R.S.

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INTRODUCTION.

EVER since the discovery of ethyl acetoacetate by Geuther in 1863, the constitution of this ethereal salt has been the subject of much discussion, and notwithstanding the fact that it has been more fully investigated than almost any other chemical compound, this question of its constitution is still disputed. This is the more remarkable when it is considered that only two formulæ can be brought forward to account for the properties of this substance, namely:—

I. $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5$.
The ketonic formula.

II. $CH_3{\cdot}C(OH){:}CH{\cdot}COOC_2H_5$.
The hydroxylic formula.

The ketonic formula was first suggested by Frankland and Duppa; the hydroxylic formula is the one which was proposed by Geuther.

The difficulty of deciding between these formulæ lies in the fact that either may be taken as almost equally well explaining the reactions of the substance, and, again, it is conceivable that it may at times act as a ketonic compound, and at others as a hydroxy-derivative; in other words, the two formulæ may be called tautomeric.

Among the latest contributions to the discussion of this question of the constitution of ethyl acetoacetate is a long and important paper by Nef (*Annalen*, **266**, 52), who, from the results of a number of interesting experiments, concludes that the hydroxylic formula is the correct one, and that the ketonic constitution, and also the idea of tautomerism, of the two formulæ must be regarded as disproved.

In support of the ketonic formula v. Pechmann brings forward a number of new arguments. He compares side by side the properties of ethyl acetoacetate and ethyl formylacetate, and argues that as these substances differ so materially in properties, they cannot be analogously constituted.

For the ethyl formylacetate, as for the ethyl acetoacetate, two formulæ are possible:—

I.	II.
$CHO·CH_2·COOC_2H_5$.	$CH(OH){:}CH·COOC_2H_5$.

The first, suggested by W. Wislicenus (*Ber.*, **20**, 2930), represents the substance as an aldehyde, and analogously constituted to the ketonic form of ethyl acetoacetate. The second, suggested by Claisen (*Sitzungsbericht d. k. Bayer Akademie der Wissenschaften*, **20**, 264), represents the substance as a derivative of vinyl alcohol corresponding to the hydroxy-form of ethyl acetoacetate, and v. Pechmann argues that from its behaviour with different reagents, it is impossible that ethyl formylacetate and ethyl acetoacetate can be analogously constituted. Having shown that ethyl formylacetate has the hydroxylic formula, he concludes that ethyl acetoacetate can only have the ketonic formula.

Claisen has likewise written a valuable paper on this subject, strongly advocating the ketonic constitution of ethyl acetoacetate (*Ber.*, **25**, 1776), and just recently Nef again refers to this subject, objecting to the arguments which have been used by v. Pechmann (*Proc. Amer. Acad.*, 1892, 160). Michael has also lately written another paper (*J. pr. Chem.*, **46**, 189), in which he calls in question the correctness of some of Nef's experiments, especially those from which he has drawn the most important conclusions.

On considering this subject, it appeared to me that it must be always a matter of great difficulty to decide definitely the constitution of substances of the nature of ethyl acetoacetate or other ketonic derivatives from the study of their chemical properties alone, more especially when it is considered that, even if they usually possess the ketonic constitution, they may in many of their reactions act in a tautomeric form, and that it would therefore be valuable if some physical method could be used which would discriminate clearly between the ketonic and hydroxylic forms of such substances.

The most important point of difference between these two classes of substances is that the ketones are saturated compounds, whereas their hydroxylic isomers are unsaturated.

To distinguish between these, the study of their refractive powers is one method which can be adopted, and Brühl (*Ber.*, **25**, 369) has lately shown that in the case of ethyl acetoacetate numbers are obtained which are in favour of the ketonic formula.

In my previous researches I have repeatedly called attention to the fact that very considerable differences are observed between the magnetic rotation of saturated and unsaturated compounds, the latter giving much larger numbers than the former, and it appeared to me that this method might in the present instance be very valuable in distinguishing between saturated ketonic substances and their unsaturated hydroxylic isomers, especially if in some cases the refractive and dispersive powers were likewise examined in confirmation of the results.

A preliminary account of some of the results in connection with this subject are published in the Proceedings of this Society (May 19, 1892, p. 100).

In the paper by Professor Claisen (*Ber.*, **25**, 1779), on the constitution of ethyl acetoacetate, already referred to, he also draws attention to my determination of the magnetic rotation of this substance, showing that this strongly favours the ketonic formula for that body.

Methods of Estimating the Magnetic Rotations.

Before considering the results I have obtained, it will be best to consider what are likely to be the differences in the rotations between these ketonic and isomeric hydroxylic compounds, and how they can best be deduced.

The difference in rotation between a saturated and an unsaturated compound of a similar kind differing by H_2 is in most cases approximately the same; in allyl compounds, however, as allyl alcohol and carboxylic compounds, with which it is associated, it is lower than in most other compounds (0·914); leaving this special case out, the following is a list of the most important comparisons between the rotations of saturated and unsaturated bodies:—

Ethyl α-crotonate and butyrate	1·112
Ethyl oleate and stearate	1·112
Methyl isobutenyl ketone (mesityl oxide), and methyl isobutyl ketone	1·145
Ethyl itaconate and glutarate............	1·120
Ethyl citraconate and glutarate	1·170
Average	1·132

In this list an exceptionally high result found between ethyl maleate and succinate, namely, 1·245, has been left out; but if this and that of an allyl compound be introduced, it will give an average which is not very different, about 1·117. In the past I have usually employed 1·112, and, as this is not far from the above, it will, I think, be best to still continue its use.

This number, 1·112, refers to the rotations of bodies differing in composition by H_2, but in the case of the ketonic and hydroxylic class of compounds under consideration this difference does not exist as they are isomeric; consequently the unsaturated or hydroxy-derivative will have a larger rotation than the ketonic by 1·112 + the value of the difference for H_2, and for dihydroxylic as compared with diketonic compounds twice this.

The value of H_2 as deduced from the rotations of the paraffins is 0·504 (Trans., 1882, **41**, 572); if this be added to the rotation of a ketonic compound, as well as 1·112, a number is obtained which approximates pretty well to that of its hydroxylic isomer. Thus:—

Mol. rot. ethyl acetoacetate..............	6·501
Difference for unsaturation by H_2...... ..	1·112
Difference for H_2.......................	0·508
	8·121

This hydroxylic compound is ethyl hydroxycrotonate, and as the rotation of ethyl crotonate is known, that of its hydroxy-derivative can be estimated probably more accurately than by the above method, by adding to it the value of OH replacing hydrogen, thus:—

Mol. rot. ethyl crotonate..................... ..	7·589
,, OH replacing hydrogen as in alcohols	0·194
	7·783

This indicates that the previous method gives numbers which are a little too high. On examination, this is found to arise from the fact that between the rotations of compounds varying in composition from each other by H_2, the difference does not amount to 0·508, but may be more or less. This is not because the value of hydrogen changes materially, but because the products are of different types, each having its own special rotation, for example, ketones differ from primary alcohols by 0·324, from secondary by 0·409, and from tertiary by 0·646. Aldehydes also differ from primary alcohols by 0·438. As this amount for the difference in composition for H_2 is a variable quantity, to find the rotations of the unsaturated hydroxylic isomers of ketonic bodies as accurately as our present information will permit, it has been found best first to ascertain the rotations of the saturated compounds corresponding to them, and then to add to these the usual amount for unsaturation by H_2, namely, 1·112. Taking ethyl acetoacetate again as an example, its isomeric unsaturated isomer, ethyl hydroxycrotonate, corresponds to the saturated compound ethyl hydroxybutyrate; then we get—

Mol. rot. ethyl hydroxybutyrate*	6·737
Difference for saturation by H_2	1·112
Ethyl hydroxycrotonate	7·849

This amount of variation between ethyl hydroxybutyrate and ethyl acetoacetate for the difference of composition by H_2 will be found to be 0·236.

It is interesting to find all the above methods give numbers which are not very wide apart, but I believe the last to be the most trustworthy.

Unfortunately, not many of the saturated compounds required have been as yet examined, and therefore it is also desirable to have some means of controlling any estimate which may be made for them, besides the ordinary method of adding or subtracting the known values of different products, and an interesting method has been found which, it will be seen, does this at any rate approximately. It is based on the system of series constants already described in this Journal (Trans., 1884, **45**, 574). From the numbers and diagrams which are given in the paper just referred to, it is seen that each series of saturated compounds has a special value of its own, and on the diagrams they will be seen to run in parallel lines, and not in one line, even where the composition is the same as in the monobasic acids and their ethyl and methyl salts. Now if from the rotation of any substance 1·023 (the value of CH_2) be taken as many times as it contains carbon atoms, the remainder is what has been called the series constant, and if the rotation of another member of the homologous series to which this compound belongs be required, it is only necessary to add to the series constant 1·023, the number of times the substance contains atoms of carbon.

With complex bodies, the use of these series constants promises to be valuable, because it is difficult to estimate by the ordinary way what will be the rotation of a substance which represents two or more classes of compounds such as ethyl lactate, which is an ethereal salt and secondary alcohol, ethyl acetoacetate, which is an ethereal salt, and a ketone, &c.

From determinations of the magnetic rotation of such compounds, it appears that their series constant is the *mean*, or very nearly so, of the series constants of the compounds they represent; thus, taking ethyl lactate, which is a secondary alcohol and ethereal salt:—

---

* The rotation of ethyl hydroxybutyrate has not yet been directly determined, but is calculated from that of ethyl lactate by the addition of the value for CH_2 (1·023). Although this is an α- and the above a β-hydroxy-compound, this is not likely to influence the estimate practically. It has been shown that the ethereal salts of tartaric and racemic acid gave the same rotations (Trans., 1887, **51**, 364). Therefore we may expect the lævo- and dextro-ethyl lactates will also have the same rotations.

Ser. const. of sec. alcohol	0·844
„ ethyl salt	0·337
	2)1·181
Estimated ser. const. of ethyl lactate	0·590
1·023 × 5	5·115
Estimated mol. rot. ethyl lactate	5·705
Found	5·720

For methyl lactate we get—

Ser. const. of sec. alcohol	0·844
„ methyl salt	0·273
	2)1·117
Estimated ser. const. methyl lactate	0·558
1·023 × 4	4·092
Estimated mol. rot. methyl lactate	4·650
Found	4·658

Ethyl acetoacetate—

Ser. const. of acetic ethereal salt	0·370
„ ketone	0·375
	2)0·745
Estimated ser. const. ethyl acetoacetate	0·372
1·023 × 6	6·138
Mol. rot. of ethyl acetoacetate	6·510
Found	6·501

Ethyl tartrate may be taken as another example. This substance represents an ethereal salt of succinic acid and a glycol,

Ser. const. of glycol	0·897
„ ethyl succinate	0·196
	2)1·093
Estimated ser. const. ethyl tartrate	0·546
1·023 × 8	8·184
Mol. rot. ethyl tartrate	8·730
Found	8·766

It is desirable in these calculations to take the series constant of the products most nearly related to the substances the rotation of which it is desired to estimate.

In this paper I have mostly used the ordinary method of finding the rotation, supplemented by this method in which series constants are employed, and have described the process somewhat in detail, so that an idea may be formed as to how far some of the curious results obtained in this investigation are to be relied upon.

Through the kindness of my chemical friends, I have had placed at my disposal for this inquiry a number of specimens of rare products; this has made it possible to examine a somewhat systematic series of substances bearing on this subject. The following is a list:—

Fatty Series.

Pyruvic acid.
Ethyl acetoacetate.
Ethyl ethylacetoacetate.
Ethyl allylacetoacetate.
× Ethyl ethylideneacetoacetate.
Levulinic acid.
†† Ethyl acetonedicarboxylate.

× * Acetylacetone.
× * Methylacetylacetone.
× Ethylacetylacetone.

× Ethyl acetonoxalate.
× Methyl acetonoxalate.
× Ethyl diacetoacetate.

† Diacetylacetone.
† Ethyl β-amidocrotonate.

Aromatic Series.

× Benzoylacetone.
Ethyl benzoylacetate.
× Methyl acetophenonoxalate.
× Ethyl acetophenonoxalate.

For the substances marked × I am indebted to the kindness of Professor Claisen, those marked † to Dr. Collie, those marked * to Professor Dunstan, and the one marked †† to Professor v. Pechmann.

It will be convenient to follow this list in the above order, to discuss the bearing of the results obtained first, and afterwards give the experimental data from which they are obtained.

THEORETICAL CONSIDERATIONS.

Pyruvic Acid.

The interest attaching to this substance is that there is but little likelihood of its possessing any other than a ketonic constitution, $CH_3 \cdot CO \cdot COOH$.

Its magnetic rotation was found to be 3·567.

If this compound be considered as acetoformic acid, its rotation, according to the series constant, would be

Ser. const. formic acid..................	0·648
„ of ketone	0·375
	2)1·023
	0·511
1 023 × 3	3·069
Estimated rot. of pyruvic acid	3·580

So that although pyruvic acid is not usually a very pure product, the rotation obtained is probably not far from correct; at any rate it is the rotation of a *saturated* compound.

Ethyl Acetoacetate.

The rotation found for this substance some years since was 6·501. I have shown when discussing the methods of calculation used in this paper (p. 806) that from the series constants it should be 6·510. That is viewing it as an acetic compound; if taken as the ether of a C_3 acid it is slightly lower, namely 6·494; the series constant for acetic ethereal salt being 0·370, whereas that of ethereal salts of monocarboxylic acids containing C_3 and upwards is 0·337.

From this agreement with the series constants and the size of the rotation, there can be no doubt that it is a *ketonic saturated* compound. Had it been an unsaturated compound, its rotation would have been about 7·849, or 1·348 higher than that found.

As a very slight internal rearrangement in the molecule of acetoacetic acid would be required for it to become an hydroxylic unsaturated body, it was thought that it would be interesting to determine its magnetic rotation at a considerably higher temperature than those previously employed, so as to see if heat were conducive to such a change.

The following is a comparison of the rotation obtained with that at ordinary temperatures:—

Mol. rot. ethyl acetoacetate at	16·2°....	6·501
„ „	90·5°....	6·470
Difference	74·3°....	0·031

The results, therefore, show that practically no change takes place when ethyl acetoacetate is heated. From observations on other substances described further on in this paper, it will be seen that this was not likely to happen, but that cooling would be more likely to have an influence in causing the formation of an unsaturated isomer. I have mentioned on previous occasions that magnetic rotations are slightly lower when determined at high than when determined at low temperatures; therefore, the above results being a little lower at 90·5° is consistent with this.

Ethyl Ethylacetoacetate.

The examination of this substance is interesting as it enables a comparison to be made with ethyl ethylmalonate, where no question as to the existence of hydroxyl can arise; the ethyl in this body being in union with carbon. Therefore if the rotation of ethyl ethylacetoacetate differs from that of ethyl acetoacetate in the same way, or approximately so, as that of ethyl ethylmalonate differs from malonate, it will be good evidence that the ethyl is in union with the carbon, thus—

$$CH_3 \cdot CO \cdot CH(C_2H_5) \cdot COOC_2H_5.$$

The rotation of ethyl ethylacetoacetate was found to be 8·329.

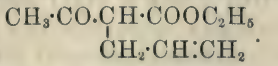
The following are the comparisons:—

Mol. rot. of ethyl ethylmalonate..........	9·272
„ malonate..............	7·410
Increase due to rep. of H in CH_2 by ethyl.	1·862
Mol. rot. of ethyl ethylacetoacetate.......	8·329
„ ethyl acetoacetate...........	6·501
	1·828

The increase in both cases is practically the same. These numbers then establish the analogy of the replacement in this compound to that in ethyl ethylmalonate, and also show that it is a *saturated* or *ketonic* compound.

Ethyl Allylacetoacetate.

This substance was examined several years ago, and was found to have a rotation of 10·382. It is an example of the introduction of an unsaturated radicle into ethyl acetoacetate by single combination, its formula being



$$\begin{array}{l} CH_3 \cdot CO \cdot CH \cdot COOC_2H_5 \\ \qquad\qquad\;\; | \\ \qquad\qquad CH_2 \cdot CH{:}CH_2 \end{array}.$$

From the following comparisons with ethyl allylacetate, it will be seen that this also has the ketonic formula:—

Mol. rot. of ethyl allylacetate............	6·426
,, ethyl acetate................	2·525
Difference due to allyl replacing H.......	3·901

Mol. rot. of ethyl allylacetoacetate.......	10·382
,, ethyl acetoacetate...........	6·501
Difference due to allyl replacing H.......	3·881

These differences are practically the same, and as ethyl allylacetate cannot contain allyl replacing the hydrogen of hydroxyl, it must be in union with the carbon; the same is evidently the case in ethyl allylacetoacetate.

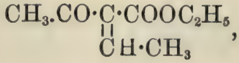
Ethyl Ethylideneacetoacetate.

This substance, which is prepared from ethyl acetoacetate and aldehyde, differs in composition from ethyl allylacetoacetate by CH_2. Its rotation was found to be 9·370. This is less than that of ethyl allylacetoacetate by practically the amount required for the difference of CH_2 (1·023).

Mol. rot. ethyl allylacetoacetate..........	10·382
,, ethyl ethylideneacetoacetate	9·370
	1·012

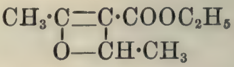
It might, therefore, be thought to be a vinyl compound, but from all we know of such bodies they do not have such a high rotation relatively as allyl compounds, that is, judging from the rotation of vinyl bromide; and on the other hand the formation of this substance from ethyl acetoacetate and aldehyde renders it improbable that it has this composition. Claisen considers it may have either of the two following formulæ:—

I.



$$\begin{array}{l} CH_3.CO\cdot C\cdot COOC_2H_5 \\ \qquad\qquad \| \\ \qquad\qquad CH\cdot CH_3 \end{array},$$

or II.



$$\begin{array}{l} CH_3\cdot C = C\cdot COOC_2H_5 \\ \qquad\quad | \qquad | \\ \qquad\quad O - CH\cdot CH_3 \end{array}.$$

It is not easy to decide between these, as both are unsaturated compounds; the first on account of its containing ethylidene replacing two hydrogens in the CH_2 group of ethyl acetoacetate, and the second on account of ethylidene replacing one hydrogen in the CH group and another in the hydroxyl group of ethyl ethylhydroxycrotonate. As this, however, represents an oxide as well as an ethereal salt, its rotation would probably be rather higher than it is. This point could probably be best decided by treating the body with nascent hydrogen. If the first formula be correct, it might yield ethyl hydroxyethylbutyrate, $CH_3{\cdot}CH(OH){\cdot}CH(C_2H_5){\cdot}COOC_2H_5$.

Levulinic Acid.

β-Acetopropionic Acid.—This acid, like acetoacetic acid and its compounds, might exist as a ketonic compound, or change into the hydroxy-unsaturated isomer, thus—

$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH.$	$CH_3{\cdot}C(OH){:}CH{\cdot}CH_2{\cdot}COOH.$
Ketonic saturated.	Hydroxylic unsaturated.

As no free acid likely to be capable of changing from a ketonic to a hydroxylic compound had been examined, and it was thought that the ethereal salt might be less mobile in this particular, the examination of the acid was undertaken. It was examined twice in the melted state, and also in aqueous solution to see whether this condition affected it in reference to its constitution. The results obtained were as follows :—

Mol. rot.	I. Fused	5·543
,,	II. ,,	5·509
,,	III. Aqueous solution	5·503
	Average	5·518

On comparing this result with the rotation of propionic acid, we get

Mol. rot. levulinic acid	5·518
,, propionic acid	3·462
Diff. = acetyl rep. hydrogen	2·056

This is very nearly the same as the value of acetyl replacing hydrogen in ethyl acetoacetate, namely, 2·039.

Calculated by series constants, it is—

Ser. const. of acid, $C_nH_{2n}O_2$	0·393
,, ketone	0·375
	2)0·768
Estimated ser. const. of levulinic acid	0·384
1·023 × 5	5·115
,, rotation of levulinic acid	5·499

This differs from the result found by only 0·019. Again, if the acid have the increment added which is necessary to give the rotation of the ethereal salt, it can be compared with ethyl acetoacetate.

Levulinic acid	5·518
Increment for ethereal salt	1·990
Ethyl levulinate	7·508
Ethyl acetoacetate	6·501
	1·007

This difference is very close to that required for CH_2, namely, 1·023. From these results, levulinic acid is seen to be a *ketonic saturated* compound.

Ethyl Acetonedicarboxylate.

The interest attaching to the examination of this substance consists in its representing ethyl acetoacetate with hydrogen of the methyl group replaced by a second ethyl carboxyl group, and as this is of a negative character, it was possible that it might influence the ketonic nature of the compound. It might exist as

$COOC_2H_5{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5$ or
Ketonic, saturated.

$COOC_2H_5{\cdot}CH{:}C(OH){\cdot}CH_2{\cdot}COOC_2H_5$.
Hydroxylic, unsaturated.

v. Pechmann, who discovered this interesting substance, has lately discussed the question of its constitution from a chemical point of view (*Ber.*, **24**, 4095), and concludes that it must possess a ketonic formula.

Brühl has also determined its refractive power, and found it to behave as a saturated compound.

Nef, on the other hand, disputes the validity of v. Pechmann's conclusions (*Proc. Amer. Acad.*, 1892, 158).

The magnetic rotation of the compound confirms to a great extent the views of v. Pechmann showing that the substance is chiefly ketonic, but it also indicates that at ordinary temperatures it also probably contains a small amount of a hydroxylic or unsaturated compound.

The rotation for the formula $COOC_2H_5{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5$ may be estimated as follows—

Mol. rot. of ethyl acetoacetate	6·501
„ $COOC_2H_5$ rep. hydrogen	2·951
	9·452

or taking acetone as the basis of the calculation,

Mol. rot. of acetone	3·514
„ $2COOC_2H_5$ rep. hydrogen	5·902
	9·416

From the series constants, it is

Ser. const. ethereal salt of bibasic acid (glutaric)	0·140
Ser. const. of ketone....................	0·375
	2)0·515
	0·257
1·023 × 9	9·207
	9·464

The first and the last calculations come very close; the average of all, 9·444, will be used in this paper.

The rotation determined at 16·5° gives 9·604 or 0·160 in excess of the calculated; this is greater than would arise from experimental error. The rotation was, therefore, again determined, but at a much higher temperature, and at 94° it gave 9·374 or 0·070 less than the calculated rotation; a result which, if its rotation at 16·5° had been about the same as the calculated, would be consistent with experience. As already mentioned in the case of ethyl acetoacetate, rotations are always slightly lower at high than at low temperatures (of course allowing for change of density).

Mol. rot. ethyl acetonedicarboxylate at	16·5°....	9·604
,, ,, ,, ,,	94·0°....	9·374
Difference	77·5°....	0·230

This difference calculated for 100° is 0·297.

This would point to some change taking place in the substance, and as will be seen farther on, indicates that any hydroxylic isomer present changes when heated into the ketonic compound, so that at 94°, and perhaps somewhat lower, it is apparently a pure ketonic product, but at ordinary temperatures contains a small quantity of a hydroxylic or unsaturated isomer.

Diketonic Compounds.

Acetylacetone, Methylacetylacetone, and Ethylacetylacetone.

Ordinary monoketones, so far as they have been examined, do not seem to have any tendency to pass into unsaturated or hydroxylic compounds. It was important, therefore, to see in what condition the so-called diketones exist at ordinary and elevated temperatures.

As monoketones might possibly change into monhydroxylic or unsaturated compounds, so diketones might change either into monhydroxyketones or into dihydroxy-derivatives or glycols, thus—

Acetylacetone	$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$,
Hydroxyketone..........	$CH_3{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH_3$,
Dihydroxy - derivative or glycol	$CH_3{\cdot}C(OH){:}C{:}C(OH){\cdot}CH_3$.

I. The rotation of *acetylacetone* may be calculated thus—

Mol. rot. of acetone	3·514
„ acetyl replacing hydrogen...	2·039
„ acetylacetone..............	5·553

In calculating diketones from series constants, the series constant of a monoketone has to be employed, because that of a diketone is not known, but possibly this is correct or nearly so, because when a second carboxyl is introduced into a compound its series constant is *lowered*, but when a second hydroxyl is introduced its series constant is *increased;* therefore, in the case of an aldehyde, or a ketone, which stands between these, it is probable that the introduction of a second ketonic group would practically not alter the series constant.

On calculating acetylacetone in this way, the following result is obtained, which goes to confirm this; the series constant of acetone being taken, as it is a derivative of that compound—

Ser. const. of acetone	0·445
1·023 × 5	5·115
Mol. rot. acetylacetone..............	5·560

This is very close to that given above.

II. The rotation of *methylacetylacetone* may be calculated on the basis of methyl ethyl ketone, this substance being in fact an acetyl derivative of the latter, thus, $CH_3{\cdot}CO{\cdot}CH(CO{\cdot}CH_3){\cdot}CH_3$.

Mol. rot. of methyl ethyl ketone	4·480
„ acetyl replacing hydrogen.	2·039
„ methylacetylacetone......	6·519

From the series constant,

Ser. const. of ketone	0·375
1·023 × 6	6·138
Mol. rot. of methylacetylacetone	6·513

These two calculations likewise agree closely.

III. The molecular rotation of *ethylacetylacetone.*

This substance may, in the same way as the above, be regarded as an acetyl methyl propyl ketone, $CH_3{\cdot}CO{\cdot}CH(CO{\cdot}CH_3){\cdot}CH_2{\cdot}CH_3$.

Mol. rot. of methyl propyl ketone	5·499
„ acetyl replacing hydrogen.	2·039
„ ethylacetylacetone	7·538

From series constants,

Ketone	0·373
1·023 × 7	7·161
Mol. rot. of ethyl acetylacetone	7·534

Before comparing the rotations found, it will be best to find the probable rotations of the isomeric monhydroxyketones.

The saturated compounds corresponding to these are—

I. Sec. acetopropyl alcohol.
II. „ acetobutyl „
III. „ acetoamyl „

The rotation found for normal acetopropyl alcohol is 5·544; if to this the difference between normal and secondary propyl alcohol be added, 0·251, the rotation of the secondary acetopropyl alcohol will be found to be 5·795, and if to this 1·112 be also added, the rotation of the hydroxyketone isomeric with acetylacetone will be obtained, viz., 6·907.

Calculating from series constants, the following results are obtained:—

I. Sec. const. isopropyl alcohol.....	0·950
„ ketone..............	0·375
	2)1·325
	0·662
1·023 × 5	5·115
Sec. acetopropyl alcohol........	5·777
For unsaturation..............	1·112
	6·889
II. Ser. const. sec. butyl alcohol	0·844
„ ketone	0·375
	2)1·219
	0·609
1·023 × 6	6·138
Sec. acetobutyl alcohol	6·747
For unsaturation..............	1·112
	7·859

III. This will be the same as II, with the addition of 1·023 or 8·882.

The dihydroxy-derivatives would be unsaturated glycols. Combes (*Bull. Soc. Chim.*, **48**, 474—483) has shown that when acetylacetone is treated with nascent hydrogen it yields amylic glycol boiling at 177°. The rotation of this and the corresponding unsaturated compound can be estimated thus—

Glycol..................	2·943
$CH_2 \times 3$	3·069
	6·012
For unsaturation × 2 ..	2·224
	8·236

The difference between the hydroxyketonic compound and the ketonic is 1·336. If this be added to the former, it will give 8·225 for the dihydroxylic compound, so that both methods of calculation practically agree. By adding this difference to the other two compounds, we get for the dihydroxylic isomers of methyl- and ethylacetyl acetone 9·295 and 10·218 respectively.

The following is a table giving a comparison of the calculated rotations as compared with those found:—

	Ketonic calc.	Hydroxy-ketonic calc.	Dihydroxylic calc.	*t.*	Found.
Acetylacetone......	5·553	6·889	8·236	16·6°	7·166
Methylacetylacetone	6·519	7·859	9·295	16·3	7·237
Ethylacetylacetone..	7·534	8·882	10·218	18·8	7·890

From this it is seen that all these substances give rotations considerably higher than those required by the ketonic constitution; that ethylacetylacetone is nearest to the calculated number for the latter; that methylacetylacetone comes nearly midway between the ketonic and hydroxyketonic constitution, and *acetylacetone* has a rotation which is even a little in excess of that required by the hydroxyketonic constitution, indicating the presence of a small quantity of dihydroxylic compound, apparently about 20 per cent.

As methylacetone has a rotation lying nearly midway between the ketonic and hydroxyketonic, it was thought possible that this substance might be a mixture of these two bodies in a state of unstable equilibrium, and that its constitution might vary with temperature. It was, therefore, measured at a much higher temperature than that at first employed, and the result confirmed this supposition, the rotation becoming considerably less. Acetylacetone and also ethylacetylacetone were likewise examined under similar conditions, and the rotations of these substances also were modified. The following are the results :—

	t.	Mol. rot.	*t.*	Mol. rot.	*t.* diff.	Mol. rot. difference.	Mol. rot. diff. for 100°.
Acetylacetone..	16·7°	7·175	93·0°	6·599	76·3°	−0·576	0·755
Methylacetylacetone	17·4	7·290	96·4	6·670	79·0	−0·620	0·785
Ethylacetylacetone	18·8	7·890	92·9	7·562	74·1	−0·328	0·443

On comparing these results with the calculated numbers in the previous table, it will be seen that ethylacetylacetone at 92·9° has a rotation which is nearly identical with that required by the *ketonic* constitution, and also that methylacetylacetone gives a number very close to that required by this kind of structure,* thus—

	Calculated ketonic.	*t.*	Found.
Acetylacetone........	5·553	93·0°	6·599
Methylacetylacetone ..	6·519	96·4	6·670
Ethylacetylacetone ..	7·536	92·9	7·562

Acetylacetone at 93° has also assumed a position between the ketonic and hydroxyketonic rotations, and thus, at this temperature, to a great extent corresponds in character to methylacetylacetone at ordinary temperatures.

Acetylacetone, after being heated, appears quickly to regain its ordinary rotation when cooled, but this is not the case with methylacetylacetone. The rotation taken at 92° was 6·675; the same specimen examined two or three hours afterwards at 15·2° gave 6·765, and had thus only increased 0·090, but when examined a few weeks afterwards, was found to have regained its normal rotation.

The density of methylacetylacetone which has been heated and then cooled is lower than it is under ordinary circumstances, or after it has rested some considerable time. The following experiment was made in reference to this. A dilatometer was quickly filled with a freshly boiled specimen of methylacetylacetone. On placing this in water at 15°, some minutes elapsed before it became stationary in the stem, some change apparently taking place; its position was then noted; in two hours it had contracted so that it was 5 mm. below its previous position, and in 24 hours it had fallen 12 mm., and it then required to be heated to 19·7° before it reached the position it originally occupied at 15°. This would correspond to a difference in density of about 0·0036. From the above results there can be no doubt that the character of these compounds changes with alterations of temperature, high temperatures favouring the ketonic or more stable condition, low temperatures the hydroxyketonic condition. It would be interesting to examine the vapours of these substances under varying conditions.

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* In making these comparisons, a small allowance of, say, about 0·100 should be added for the influence of temperature on the rotation made at the higher temperature; this will slightly reduce the difference of rotation.

To confirm the interpretation given of the remarkable rotation of these bodies, the refractive and dispersive powers of two of them were examined at different temperatures. The refractive power should, like the rotation, show whether they are saturated or unsaturated compounds, becoming less with rise of temperature as they become saturated; and as the dispersion should also become less as they pass from saturated towards unsaturated compounds, this would give additional evidence if there were a change. The full details are given in the Experimental Part of this paper. The following numbers for three lines will show the results :—

Refraction and Dispersion of Acetylacetone at Temperatures wide apart.

	$t.$	$\frac{\mu_A - 1}{d} p.$	$\frac{\mu_F - 1}{d} p.$	$\frac{\mu_G - 1}{d} p.$
	11·0°	45·17	47·46	48·72
	99·3°	44·14	46·12	47·17
Reduction from rise of temperature...	88·3°	1·03	1·34	1·55

The refractive power of this substance at ordinary temperatures is remarkably high. For the unsaturated compound it should be 42·2; with Brühl's estimate for one ethylene combination = 2·30, it would be 44·5, and for two, 46·8; so, like the rotation, this shows that it is the hydroxyketone containing some dihydroxy-derivative. To be sure these results were correct, I asked Dr. Gladstone if he would also examine this substance, and he was kind enough to do so; he used Dr. Claisen's specimen, whereas I employed Professor Dunstan's, and obtained :—

$t.$	$\frac{\mu_A - 1}{d} p.$	$\frac{\mu_F - 1}{d} p.$	$\frac{\mu_H - 1}{d} p.$
18·4°	45·62	47·99	50 70

These confirm the foregoing. Dr. Gladstone remarks—" That the molecular refraction observed is higher than the theoretical, but only to an extent that might be explained on the supposition of the substances being unsaturated; thus acetylacetone, if it contained two double bonds, would give, theoretically, 45·4.* 2nd. That the dispersion is enormous and far beyond anything that can be accounted for by the double linking." In my results the dispersion between A and G amounts to no less than 3·55, and Dr. Gladstone found, between A and H, 5·08, whereas the theoretical, even considering the substance as doubly unsaturated, would only amount to about 3·58 between A and H.

From the results obtained at 99·3°, it is seen that the refraction has fallen by heating to this temperature, 1·02 for the A line and 1·55 for the G line; therefore the dispersion has altered to the exten of the difference between these numbers, namely, 0·53; this is between A and G; between A and H it would be considerably more, approaching double this amount. The refraction and dispersion, therefore, support the conclusions arrived at from the magnetic rotation.

Refraction and Dispersion of Methylacetytacetone at Temperatures wide apart.

The following results were obtained :—

	$t.$	$\frac{\mu_A - 1}{d} p.$	$\frac{\mu_F - 1}{d} p.$
	8·3°	50·81	52·75
	99·2°	49·88	51·56
Reduction from rise of temperature ..	90·9°	00·93	1·19

The refractive power is in this case too high for the ketonic or unsaturated compound, which would require 49·8, and it is too low for the unsaturated, which, by adding 2·30 on to the last number, would be 52·1; this accords with the magnetic rotation, showing that this substance is a mixture of the ketonic and hydroxyketonic compounds, and when heated to 99·2° it also gives numbers showing that at this temperature it is practically ketonic. This change is also accompanied by a reduction of the dispersion, as would be expected, but rather less than in the case of acetylacetone; it amounts to 0·26 between A and F. The dispersion of this substance at ordinary temperatures is high.

It appears, then, that when acetylacetone, which is, from its rotation, at ordinary temperatures a hydroxyketonic compound apparently containing a small quantity of a dihydroxy-isomer, is methylated or ethylated, it becomes a mixture of ketonic and hydroxyketonic compounds.

---

* Taking Bruhl's numbers, this would not be high enough for two ethylene combinations.

As the ethylic is more ketonic than the methylic derivative, it would appear that, the larger the hydrocarbon radicle introduced, the greater the tendency of the substance to become ketonic.

Ethyl Acetoneoxalate or Ethyl Acetylpyruvate.

This substance was discovered by Claisen and Stylos (*Ber.*, **20**, 2188—2191), by acting on ethyl oxalate with sodium alcohol and acetone. This may be regarded as acetylacetone in which methyl is replaced by $COOC_2H_6$, and its examination was important, because in the case of ethyl acetoacetate the replacement of a second hydrogen by $COOC_2H_5$, and consequent formation of ethyl acetonedicarboxylate, appeared to influence the ketonic group and cause the formation of a small amount of a hydroxylic compound. Therefore, if the methyl in acetylacetone—which, at ordinary temperatures, exists as the isomeric hydroxyketonic compound—is replaced by this group, $COOC_2H_5$, it might be further influenced, and changed, partly or entirely, into a dihydroxy-derivative.

The magnetic rotation for the ketonic compound

$$CH_3\cdot CO\cdot CH_2\cdot CO\cdot COOC_2H_5$$

may be calculated thus :—

Mol. rot. of ethyl pyruvate..........	5·504
,, acetyl replacing H	2·037
	7·541

Calculating from series constants—

Ser. const. ethereal salt	0·337
,, ketone × 2..............	0·750
	3)1·087
	0·362
1·023 × 7	7·161
	7·523

Average, 7·532.

The monhydroxylic compound would be

$$CH_3\cdot CO\cdot CH:C(OH)\cdot COOC_2H_5 \text{ or } CH_3\cdot C(OH):CH\cdot CO\cdot COOC_2H_5;$$

both of these would probably have the same or nearly the same rotation. Taking the first, the saturated compound corresponding to this is ethyl hydroxylevulinate, $CH_3\cdot CO\cdot CH_2\cdot CH(OH)\cdot COOC_2H_5$. Its rotation would be :—

Mol. rot. of ethyl levulinate	7·519
OH	0·194
,, ethyl hydroxylevulinate	7·713
For unsaturation	1·112
	8·825

From series constants—

Ser. const. secondary alcohol	0·844
,, ethereal salt	0·337
,, ketone	0·375
	3)1·556
	0·519
1·023 × 7	7·161
Ethyl hydroxylevulinate	7·680
For unsaturation	1·112
	8·792

Average, 8·809.

The dihydroxylic compound would be

$$CH_3{\cdot}C(OH){:}C{:}C(OH){\cdot}COOC_2H_5;$$

and the saturated compound corresponding to it,

$$CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}COOC_2H_5,$$

or butyl glycol with hydrogen replaced by $COOC_2H_5$. The rotation can then be calculated thus:—

Mol. rot. of butyl glycol (calculated)	4·989
,, $COOC_2H_5$ replacing H	2·950
For unsaturation × 2	2·224
	10·163

The difference between the estimated rotation of the ketonic and hydroxyketonic compounds is 1·277; if this be added to the rotation of the latter it gives 10·085 for the rotation of the dihydroxy-compound. These calculations are not quite so concordant as usual; their mean is 10·124, which will probably be not far from the truth.

The molecular rotation of ethyl acetoneoxalate is 10·122, which is very close to the above; therefore the substance has the *dihydroxy-*constitution $CH_3{\cdot}C(OH){:}C{:}C(OH){\cdot}COOC_2H_5$.

Its rotation was also determined at a higher temperature, and the following is a comparison of the different results obtained:—

	t.	Mol. rot.	*t.*	Mol. rot.	*t.* diff.	Mol. rot. diff.
Ethyl acetoneoxalate	19·9°	10·122	89·5°	9·82	69·6°	0·302

For 100° the difference would be 0·434. This shows a reduction of rotation much greater than could result from the influence of temperature alone, and therefore indicates an alteration of a portion of the substance into the hydroxyketonic compound.

The determination of the refractive power of this substance points to the same conclusion. This was determined by myself and also by Dr. Gladstone; the detailed results will be found further on, but the following numbers will show this:—

		$\frac{\mu_A - 1}{d}p.$	$\frac{\mu_F - 1}{d}p.$	$\frac{\mu_H - 1}{d}p.$
Perkin....	17·0°	65·091	68·593	—
	100·0°	64·676	68·096	—
Diff. ..	83·0°	0·415	0·497	
Gladstone	22·1°	65·28	68·78	72·89

If a saturated compound, the calculated values for A would be 60·4, with a dispersion of 2·78 between A and H. With two ethylene linkings (Brühl), it would be 65·0 for A, which is close to that found. The reduction of the refraction and dispersion on heating, though not much greater than would be expected from the action of heat alone (see this vol., pp. 293, 310), tends to confirm the conclusion, namely, that this substance alters in constitution slightly, a small portion changing into the hydroxyketonic compound.

Methyl Acetoneoxalate or Methyl Acetylpyruvate.

As this substance is solid at ordinary temperatures, it had to be examined in the melted condition; it fuses at 63—64°; being a methyl salt, its rotation should differ from that of the ethyl salt by about 1·100 less; this would make it—

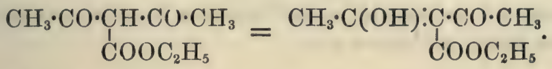
For ketonic compound..........	6·432
„ hydroxyketonic compound...	7·709
„ dihydroxy-compound........	9·024

The rotation obtained at 66° was 8·876. Therefore at this temperature the rotation is close to that required by the dihydroxy-compound, though not quite high enough. But if the rotation of this substance changes with heat to the same extent as that of the ethylic compound, at 20° it would be 9·075, which is close to the estimated number, so that this substance has also the dihydroxylic constitution

$$CH_3\cdot C(OH)\colon C\colon C(OH)\cdot COOCH_3.$$

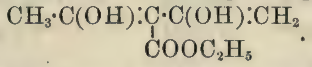
Ethyl Diacetoacetate.

This substance, which may be regarded as acetylacetone with hydrogen replaced by the group $COOC_2H_5$, as well as ethyl diacetoacetate, has special interest in reference to the subject under consideration. It has been shown from the rotations of acetylacetone at ordinary temperatures that it is a monhydroxy-compound, and as its rotation is rather higher than is required by that constitution, it may be assumed that it has a tendency to become a dihydroxy-compound. On replacing one of its methyls by $COOC_2H_5$, and thus producing ethyl acetoneoxalate, this tendency is increased, and a dihydroxy-compound is formed; therefore, if, instead of replacing a methyl group, we replace one of its hydrogen atoms by $COOC_2H_5$, somewhat analogous conditions are obtained which would also be expected to conduce to the formation of a dihydroxy-compound, but in this case a hydrogen of the central CH_2 is replaced; this, therefore, can now only lend one hydrogen to one of the —CO— groups, and thus only a monhydroxy-compound can be formed in the ordinary manner.



$$\underset{\textstyle COOC_2H_5}{CH_3{\cdot}CO{\cdot}\overset{}{C}H{\cdot}CO{\cdot}CH_3} = \underset{\textstyle COOC_2H_5}{CH_3{\cdot}C(OH){:}C{\cdot}CO{\cdot}CH_3}.$$

If a dihydroxy-compound were formed, it would therefore be necessary for one of the methyl groups to give up hydrogen to the carbonyl and produce



$$\underset{\textstyle COOC_2H_5}{CH_3{\cdot}C(OH){:}C{\cdot}C(OH){:}CH_2}.$$

The rotation of this substance may be estimated thus:—

Mol. rot. ethyl acetoacetate..........	6·501
,, acetyl rep. hydrogen........	2·037
,, ketonic compound..........	8·538
Calculated from series constant—	
Ser. const. ketone × 2..............	0·750
Ethereal salt	0·370
	3)1·120
	0·373
1·023 × 8	8·184
Mol. rot. ketonic compound..........	8·557

Average 8·547.

To find the rotation for the monhydroxyketonic and dihydroxylic compounds the same difference of 1·277 can be used as in the case of acetoneoxalethyl ether.

Thus—

Mol. rot. ketonic compound............	8·547
	1·277
„ monhydroxyketonic compound..	9·824
	1·277
„ dihydroxylic compound........	11·101

The rotation found at 18·4° was 10·699. This is considerably too high for a monhydroxyketonic compound, the difference being 0·875, whereas it is only 0·402 lower than that required by the dihydroxylic compound; in fact, it appears to consist of about one-third of the former and two-thirds of the latter compound.

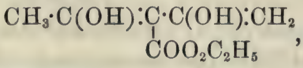
When heated to 92·6°, its rotation was 10·449, being a reduction of 0·250 for 74·2° or 0·337 for 100°. This is larger than is likely to result from the influence of heat alone, showing that a change takes place, the quantity of the monhydroxyketonic compound present becoming slightly larger.

The determinations of the refractive power of this substance made by Dr. Gladstone and also by myself confirm the above results, as the following numbers will show:—

	$t.$	$\frac{\mu_A - 1}{d}p.$	$\frac{\mu_F - 1}{d}p.$	$\frac{\mu_H - 1}{d}p.$
Perkin....	17·6°	71·952	75·030	—
	99·8°	71·641	74·666	—
Diff. ..	82·2°	0·311	0·364	
Gladstone	22·8°	71·91	75·27	78·65

Dispersion H—A = 6·774.

If a saturated compound, the calculated value for A would be 68·0, with a dispersion of 3·12 between A and H. With one ethylene linking (Brühl), it would be 70·3, and for two 72·6. The refractive power, therefore, like the rotation, shows that it consists of a mixture of a mono- and di-hydroxylic compound; the dispersion is even in excess of that required by this constitution, and this is further indicated by the reduction of the refraction and also of the dispersion on heating, which, however, is not much greater than might arise from the action of heat.

These results, therefore, indicate the unexpected existence of the compound  $CH_3{\cdot}C(OH){:}\underset{COO_2C_2H_5}{C}{\cdot}C(OH){:}CH_2$, as forming the chief constituent of ethyl dioacetacetate at ordinary temperatures.

Diacetylacetone.

This substance might exist in four conditions, or, in other words, have three isomers :—

I. Triketonic	$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$.
II. Hydroxydiketonic	$CH_3{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$.
III. Dihydroxyketonic	$CH_3{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CH_3$.
IV. Trihydroxy-	$CH_3{\cdot}C(OH){:}C{:}C(OH){\cdot}CH{:}C(OH){\cdot}CH_3$.

The rotation may be estimated as follows :—

I. *Triketonic formula*—

Mol. rot. of acetone	3·514
" acetyl rep. hydrogen × 2	4·074
	7·588

According to series constant—

Ser. const. acetone × 3 ÷ 3	0·445
1·023 × 7	7·161
	7·606

Average 7·597.

II. *Hydroxydiketonic Formula.*—The saturated form of this would be $CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, or acetylmethyl hydroxypropyl ketone.

Methyl propyl ketone may, therefore, be taken as the basis.

Mol. rot. of methyl propyl ketone	5·499
" acetyl replacing hydrogen	2·037
	7·536
OH	0·194
	7·730
For unsaturation	1·112
	8·842

By series constant, the saturated compound being viewed as an isopropyl alcohol derivative,

Ser. const. isopropyl alcohol	0·950
„ ketone × 2..........	0·750
	3)1·700
	0·566
1·023 × 7	7·161
	7·727
For unsaturation	1·112
	8·839

Average, 8·840.

III. *Dihydroxyketonic Formula.*—The saturated form of this would be $CH_3·CH(OH)·CH_2·CO·CH_2·CH(OH)·CH_3$. This is a dihydroxydipropyl ketone.

Taking dipropyl ketone as the basis of the calculation, the following result is obtained:—

Mol. rot. of dipropyl ketone	7·536
$(OH)_2$ 194 × 2........	0·398
	7·934
For unsaturation × 2 ..	2·224
	10·158

By series constant, regarding the saturated compound as a ketonic dimethyl glycol,

Ser. const. dimethyl glycol (calc.)	1·078
„ ketone..............	0·375
	2)1·453
	0·726
1·023 × 7	7·161
	7·887
For unsaturation × 2.	2·224
	10·111

Average, 10·134.

IV. *Trihydroxylic Formula.*—The saturated form of this would be $CH_3·CH(OH)·CH_2·CH(OH)·CH_2·CH(OH)·CH_3$. This is a heptane glycerol.

Mol. rot. of heptane glycerol (calc.) ..	8·204
For unsaturation × 3..	3·336
	11·540

If the difference of 1·277 found between similar formulæ in some of the calculations be used, the numbers obtained are not very different to the above.

I. Triketone	7·597
	1·277
II. Hydroxydiketone	8·874
	1·277
III. Dihydroxyketone	10·151
	1·277
IV. Trihydroxy-	11·428

The last is the least concordant, differing by 0·112.

As diacetylacetone is a solid, it was examined in the fused state at 60·4°; it then gave 10·223 for its molecular rotation. This evidently agrees nearly with III or the dihydroxyketonic constitution

$$CH_3{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CH_3,$$

though it is even a little high for this.

The rotation was also determined at 96·3°, and then gave 9·587 for its molecular rotation, which shows a very large reduction considering the temperature is only 36·4° above the previous number, thus:—

t.	Mol. rot.	*t.*	Mol. rot.	*t.* diff.	Mol. rot. diff.
59·3°	10·223	96·3°	9·587	37·3°	0·635

For 100°, supposing the change to take place equally (which is improbable, as it is likely to become more rapid as the temperature rises), it would amount to 1·704.

From this it will be found that if heated up to about 137° it would have passed into II, the hydroxydiketonic compound, with a rotation of 8·874, and if it could be kept liquid whilst cooled to about −6·7° it would have passed into IV, the trihydroxy-compound, with a rotation of 11·428.

The refraction and dispersion powers of this substance were determined at two different temperatures; the following numbers show the result:—

	t.	$\frac{\mu_A - 1}{d}p.$	$\frac{\mu_F - 1}{d.}p.$
	60·0°	63·599	67·509
	99·8°	62·643	66·180
Diff. ..	39·8°	0·956	1·329

The calculated refraction for A, if a saturated compound, would be 58·2, but with two ethylene linkings (Brühl) 62·80. This is somewhat lower than that obtained, but for three ethylene linkings it would be 65·1, which is too high; therefore these results show, like the rotation, that it is a dihydroxylic compound at this temperature. As with the rotation, the effect of heat on this substance alters it to a very large extent, both in refraction and dispersion. The above differences are only for about 40°; for 100° they would be 2·402 and 3·417 respectively, giving a difference of dispersion of no less than about 1·015.

Ethyl β-Imidobutyrate, or Ethyl β-Amidocrotonate.

This substance, which is known by both the above names, is produced by the action of ammonia on ethyl acetoacetate; its constitution is, however, disputed, some regarding it as having that represented by the first name, and others as corresponding to the second name.

The constitution indicated by the first name, namely,

$$CH_3{\cdot}C(NH){\cdot}CH_2{\cdot}COOC_2H_5,$$

is explained very easily if the reaction be taken as occurring between ammonia and ethyl acetoacetate, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5$. In this case it would be a saturated compound; but if it be indicated by the second name, that is, $CH_3{\cdot}C(NH_2){:}CH{\cdot}COOC_2H_5$, its formation is most easily explained by taking ethyl acetoacetate as $CH_3{\cdot}C(OH){:}CH{\cdot}COOC_2H_5$. In this form it would be an unsaturated compound. It was, therefore, interesting to examine the rotation of this substance.

Its rotation may be estimated thus:

I. As ethyl imidobutyrate—

Mol. rot. of ethyl butyrate	6·477
Less H	0·254
	6·223
Plus nitrogen in amines	0·717
,, ethyl imidobutyrate	6·940

II. As ethyl amidocrotonate—

Mol. rot. of ethyl α-crotonate	7·589
NH_2 rep. H	0·971
,, ethyl amidocrotonate	8·560

The rotation of the substance in a state of surfusion at 15° was 10·770; it was also examined at 86·5°, and gave 10·494, giving a difference of 0·276 for 71·5°; but it would not be wise to lay much stress upon this, as, when kept heated, this substance undergoes decomposition very quickly with evolution of ammonia.

The rotation found is no less than 2·210 higher than that estimated, even for the unsaturated compound; so that there cannot be a doubt that it is a compound of that nature; but why it is so abnormally high it is difficult to understand. Very little, however, is known as to the rotation of unsaturated amido-derivatives (allylamine being the only one examined; this, however, does not give an abnormal rotation), but that the NH_2 has a remarkable influence, in some instances, is certain; this is seen in the aromatic series, where aniline and other bases are found to give remarkably high rotations. For example, benzene has a rotation of 11·295; the introduction of NH_2 and formation of aniline raises this to 16·097. Therefore the method of estimating the rotation of this substance may be at fault to some extent. It also might possibly be that this compound is a fumaroïd modification; this would raise the rotation, but not sufficiently to account for all the difference found.

On account of obtaining these high numbers, it was thought desirable to examine the refractive power of this substance; this gave for

t.	$\frac{\mu_A - 1}{d} p$.	$\frac{\mu_G - 1}{d} p$.
16°	61·67	67·08

The substance was then allowed to crystallise, and well pressed between bibulous paper to remove any changed product it might contain from having been heated a little; it then gave—

t.	$\frac{\mu_A - 1}{d} p$.	$\frac{\mu_G - 1}{d} p$.
15·8°	61·80	67·17

These two determinations thus give practically the same results.

These numbers, like the rotation, are remarkably high. The calculated values, $C_6H_{11}NO_2$, are—

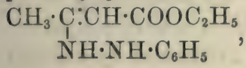
As saturated	55·5
As unsaturated	57·8

The dispersion G—A is 5·37, which is enormous.

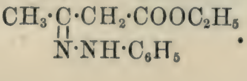
The refractive and dispersive powers, therefore, confirm the magnetic rotations.

Had it not been known that ethyl acetoacetate was a ketonic compound, the formation of this substance might have been considered as favouring its hydroxylic constitution.

The action of ammonia on ethyl acetoacetate is analogous to that of phenylhydrazine, as Nef has shown (*Annalen*, **266**, 64) that the primary product formed in the latter case is the phenylhydrazide,



$CH_3{\cdot}\underset{\displaystyle NH{\cdot}NH{\cdot}C_6H_5}{\underset{|}{C}}{:}CH{\cdot}COOC_2H_5$, and not the phenylhydrazone,



$$CH_3{\cdot}\underset{\displaystyle N{\cdot}NH{\cdot}C_6H_5}{\underset{||}{C}}{\cdot}CH_2{\cdot}COOC_2H_5.$$

Aromatic Compounds.

The examination of the following compounds, which correspond to some of the foregoing, in which methyl is replaced by phenyl, namely:—

- Ethyl benzoylacetate,
- Benzoylacetone,
- Methyl acetophenoneoxalate,
- Ethyl acetophenoneoxalate,

is interesting, because the introduction of phenyl into a compound affects its properties in a different way from that of the alcohol radicles, being less basic in its character.

The magnetic rotations of a very large number of aromatic compounds have been determined but not yet published, and thus some help can be obtained in calculating the rotations the above substances should have. No set of series constants has as yet been formed, so that this means of corroborating the numbers obtained by other methods cannot be used, but, as the differences to be dealt with are large, any small errors will not invalidate the conclusions arrived at.

In the aromatic series, the average value of C_6H_5 replacing hydrogen is 10·400. This, however, fluctuates; thus in ethyl benzoate it is 10·301, in acetophenone 10·122, and in benzyl alcohol 10·760.

The difference between the rotation of saturated and unsaturated compounds containing C_6H_5 is much greater than in the fatty series. The following comparisons will show this:—

	Mol. rot.	Diff.
Cinnamene	16·081	2·690.
Ethylbenzene	13·391	
Allylbenzene	17·577	3·027.
Propylbenzene........	14·550	
β-Butenylbenzene	18·325	2·735.
Butylbenzene (calc.) ..	15·590	
The average of these is		2·817.

This value is for substances differing in composition by H_2. But the above ketonic compounds and their unsaturated hydroxylic isomers do not differ in composition by H_2, so that this will have to be taken into account.

The difference of rotation due to the variation of composition by H_2 in the aromatic series, which would apply to the calculation of the rotation of the unsaturated hydroxylic compounds under consideration, cannot be obtained directly, but may be arrived at by analogy from the fatty series, thus—

The rotation of benzylic alcohol is 12·400, and that of benzaldehyde 11·846; the difference between these rotations for variation of composition by H_2 is 0·554.

If we compare aldehydes and alcohols in the fatty series, the difference found is about 0·436.

In the fatty series the amount for unsaturation by H_2 (1·112) will be found to have required the addition of 0·224 to make it suitable to represent the difference for unsaturation in the case of the hydroxylic isomers of ethyl acetoacetate and acetylacetone, and 0·165 in the case of the monohydroxylic isomers of ethyl and methyl acetoneoxalate.

Now, as the difference between alcohols and aldehydes of the fatty series is to the above quantities, so will most probably be the difference between the aromatic alcohols and aldehydes to the numbers required.

For ethyl benzoylacetate and benzoylacetone this would be 0·284; this, added to the amount for unsaturation, namely, 2·817, will give 3·101 as the difference in rotation which exists between the rotation of these two substances and their hydroxylic unsaturated isomers. For ethyl and methyl acetophenoneoxalate it will be 0·209; this, with 2·817, will give 3·026 as the difference for this class of compound.

The influence of $COOC_2H_5$ and $COOCH_3$ replacing hydrogen in the aromatic series is about 2·800 and 1·340 respectively.

The value of CH_2 is slightly higher than in the fatty series, namely, 1·040.

With these particulars it will be possible to get pretty close approximations to the molecular rotation of the substances under consideration and their possible hydroxylic isomers.

Ethyl Benzoylacetate.

The rotation of this compound and its unsaturated hydroxylic isomer may be calculated thus:—

Mol. rot. of ethyl acetoacetate..........	6·501
Less CH_2	1·023
	5·478
,, phenyl replacing hydrogen as in acetophenone........	10·122
,, ethyl benzoylacetate...	15·600
For unsaturation	3·101
Hydroxylic compound	18·701

The molecular rotation found for ethyl benzoylacetate was 16·393 at 18·8°; this is higher than that required by the ketonic constitution by 0·793, but less than is required by the hydroxylic constitution by 2·321; it would, therefore, appear to be a mixture consisting of about 3 parts of the ketonic to 1 of the hydroxylic compound. This substance was, therefore, measured at a higher temperature, namely, 100·6°, and it then gave 16·192 (corrected for influence of temperature; see p. 862). The following shows clearly this influence of temperature:—

t.	Mol. rot.	*t.*	Mol. rot.	*t.* diff.	Mol. rot. diff.	Diff. 100°.
18·8°	16·393	100 6°	16·191	81·8°	0·202	0·247

These results indicate that this substance becomes somewhat more ketonic in composition by rise of temperature in the same way as do many of the fatty compounds previously examined.

From the rotation of ethyl benzoylacetate it is seen that phenyl favours the hydroxylic condition more than methyl, because ethyl acetoacetate appears to be ketonic only.

Benzoylacetone.

This substance, which is the phenylic representative of acetylacetone, may also be regarded as acetylacetophenone,

$$CH_2(CO{\cdot}CH_3){\cdot}CO{\cdot}C_6H_5.$$

Its rotation and that of its hydroxylic isomers may be estimated thus:—

Mol. rot. of acetophenone	12·591
,, acetyl rep. H	2·039
,, benzoylacetone	14·630
For unsaturation	3·101
,, hydroxyketonic compound	17·731
For unsaturation	3·101
,, dihydroxylic compound	20·832

Benzoylacetone melts at 58°. Its rotation was determined at 63·3°, and gave 18·782. It is evidently nearest to that of the hydroxyketonic compound, $CH_3{\cdot}CO{\cdot}CH{\colon}C(OH){\cdot}C_6H_5$, but at the same time it is 1·039 above that number, indicating that it contains about 30 per cent. of the dihydroxylic compound, $CH_3{\cdot}C(OH){\colon}CH{\colon}C(OH){\cdot}C_6H_5$. Acetylacetone was found to consist of a hydroxyketonic compound with about 20 per cent. of the dihydroxylic compound. This comparison again shows that phenyl favours the hydroxylic condition more than methyl does.

Methyl Acetophenoneoxalate.

This substance corresponds to methyl acetoneoxalate, in which a methyl group is replaced by phenyl; its composition is

$$C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}COOCH_3.$$

It may be viewed as benzoylacetone in which methyl is replaced by $COOCH_3$, and its rotation estimated for its ketonic and hydroxylic forms; thus:—

Mol. rot. of benzoylacetone	14·630
Less CH_2	1·040
	13·590
„ $COOCH_3$ rep. H	1·340
„ methyl acetophenoneoxalate	14·930
For unsaturation..........	3·026
„ hydroxyketonic compound..	17·956
For unsaturation..........	3·026
Dihydroxylic compound....	20·982

This substance melts at 61°. Its rotation was determined in the fused state at 66·5,° and gave 21·511. This agrees nearest with that of the dihydroxy-compound, $C_6H_5{\cdot}C(OH){:}C{:}C(OH){\cdot}COOCH_3$; it is, however, a little higher (0·529); but as there is no probability of a trihydroxy-compound existing, and much difficulty was experienced in determining its rotation, this may be due to experimental error.

The result agrees with that obtained with methyl acetoneoxalate.

Ethyl Acetophenoneoxalate.

The rotations of this substance for the three forms in which it might exist should be about 1·100 higher than for the methyl salt. This would give the following numbers:—

Mol. rot. for ketonic compound	16·030
„ hydroxyketonic compound	19·056
„ dihydroxylic compound.	22·082

This substance, which melts at 42°, was examined at 47·1°, and gave for its molecular rotation 22·175. This again is for the dihydroxylic constitution $C_6H_5\cdot C(OH)\dot{:}C\dot{:}C(OH)\cdot COOC_2H_5$, ethyl acetoneoxalate also giving numbers for an analogous compound.

Conclusions.

Monoketonic Compounds.—With the exception of ethyl acetonedicarboxylate, all those which have been examined for their magnetic rotation, as well as for their refractive power (where this has been observed), are shown to be saturated, and therefore ketonic. In the case of ethyl acetonedicarboxylate, a small quantity of a hydroxylic compound is apparently present owing to the influence of the two negative $COOC_2H_5$ groups, which are seen to have such a large influence in other cases.

Besides the compounds examined in this paper, this has also been found to be the case in the following instances:—

Ethyl acetosuccinate,
Acetobutyl alcohol,
Acetopropyl alcohol,
Acetylcarbinol,
Dichloracetone,
Acetylmethylpentamethylene.

Diketonic Compounds.—Acetylacetone at about 17° is found to be, both by its magnetic rotation and refractive power, an unsaturated hydroxyketonic compound containing about 20 per cent. of a dihydroxylic compound.

Methyl and ethyl acetoneoxalate, which differ from the foregoing in containing the positive groups $COOCH_3$ and $COOC_2H_5$ in place of methyl, are dihydroxylic at about 20°.

Ethyl diacetoacetate at 18° consists of a mixture of about 32 per cent. of monhydroxylic and 68 per cent. of dihydroxylic compounds.

Triketonic Compounds.—The only one of these examined, namely, diacetylacetone, when fused, is at about 60° a dihydroxylic compound.

From the rotation of methyl- and ethyl-acetylacetone, it appears that the alcohol radicles replacing hydrogen in acetylacetone, render the compound more ketonic, the larger radicle having the greater influence in this respect; thus the composition of these bodies at ordinary temperatures may be represented:—

	Per cent. of ketonic.	Per cent. of hydroxylic.	Per cent. of dihydroxylic.
Acetylacetone........	—	80·0	20
Methylacetylacetone ..	46·4	53·6	—
Ethylacetylacetone ..	74·0	26·0	—

From this it may be inferred that, if still larger radicles were introduced, it is probable that the hydroxyketonic compound would cease to exist, and the body be simply ketonic.

This has an important bearing upon the subject of judging as to what the constitution of compounds of this class will be from those they are derived from, or *vice versâ.* For example, both these substances are produced from unsaturated acetylacetone,

$$CH_3{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH_3,$$

or from its sodium compound, $CH_3{\cdot}C(ONa){:}CH{\cdot}CO{\cdot}CH_3$; yet ethylacetylacetone consists chiefly of the saturated ketonic product $CH_3{\cdot}CO{\cdot}CH(C_2H_5){\cdot}CO{\cdot}CH_3$.

From this it is seen that the presence of hydrocarbon radicles of the fatty series favours the ketonic form, just as the positive radicle $COOC_2H_5$ favours the hydroxylic form.

The magnetic rotations of the aromatic compounds confirm those obtained with the corresponding compounds in the fatty series, but, at the same time, phenyl being a more positive compound than methyl, the hydroxylic condition is favoured to a greater extent, even ethyl benzoylacetate containing apparently about 20 per cent. of its hydroxylic isomer.

Ethyl acetoacetate, being a ketonic compound, is not changed when heated, but the small amount of hydroxylic isomer present in ethyl acetonedicarboxylate disappears below 100°.

Ethyl β-imidobutyrate or β-amidocrotonate is evidently an unsaturated compound, and, therefore, is correctly described by the second name.

All the diketonic compounds of the fatty series examined are more or less hydroxylic, and change when heated, becoming less hydroxylic, acetylacetone and methylacetylacetone being the most largely affected. This is also true of ethyl benzoylacetate, and probably the other aromatic compounds examined.

The triketone diacetylacetone changes to a much greater extent than any of the other substances examined with rise of temperature, becoming less hydroxylic.

It is seen from the above observations that the influence of heat on the hydroxylic isomers of the ketonic compounds tends to cause them to change into the more stable ketonic form.

The existence of products consisting of two or more isomeric compounds in a state of unstable equilibrium, their relative proportions varying with temperature, is remarkable, especially as they differ considerably in constitution, some being saturated, and others unsaturated: so that it is difficult to tell why the presence of one should be necessary to the existence of the other or others. This may have something to do with the way these products behave with reagents, because it is just possible that the addition of other substances may disturb the equilibrium that exists, and the product may become either entirely, or to a much larger extent, ketonic, or (which is less probable) hydroxylic, and this may account for results obtained which are different from those expected.

It would, therefore, be interesting to examine the magnetic rotations of mixtures of some of these compounds, such as acetylacetone, with different reagents, as this would show whether they do have any influence of this kind. I hope to do this when I have the opportunity. When high temperatures are employed to induce chemical change, it is well to remember that these substances will probably, in many cases, be ketonic compounds.

Experimental Results.

Pyruvic Acid.

The acid was obtained from Kahlbaum; as the purity of the acid is always doubtful, however carefully prepared, it was examined by titration with sodium hydrate solution. The result obtained showed 99·89 per cent. of acid.

The density determinations gave—

d 4°/4° 1·2881.
d 10/°10° 1·2808.
d 15°/15° 1·2752.
d 20°/20° 1·2700.
d 25°/25° 1·2649.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
14·5°	0·9282	3·557
14·5	0·9279	3·556
14·5	0·9294	3·561
14·5	0·9272	3·553
Average 14·5	0·9282	3·557

Ethyl Acetoacetate.

The boiling point of the specimen used was 181—182° (corr.).

The density determinations gave—

d 70°/70° 0·9941.
d 75°/75° 0·9913.
d 80°/80° 0·9888.
d 85°/85° 0·9865.
d 90°/90° 0·9843.
d 95°/95° 0·9824.
d 100°/100° 0·9809.

The magnetic rotations gave—

	t.	Sp. rotation.	Mol. rotation.
	90·5°	0·8894	6·527
	90·5	0·8817	6·470
	90·5	0·8774	6·439
	90·5	0·8801	6·459
	90·5	0·8789	6·450
	90·5	0·8824	6·476
Average	90·5	0·8816	6·470

Ethyl Ethylacetoacetate.

This was prepared from ethyl sodacetoacetate and ethyl iodide in the usual manner. It boiled at 197·7—198·8° (corr.).

The density determinations gave—

d 4°/4°	0·9937.	*d* 15°/15°	0·9838.
d 10°/10°	0·9879.	*d* 20°/20°	0·9800.
d 25°/25°	0·9767.		

The magnetic rotations gave—

	t.	Sp. rotation.	Mol. rotation.
	17·8°	0·9286	8·304
	17·8	0·9333	8·346
	17·8	0·9308	8·324
	17·8	0·9304	8·320
	17·8	0·9348	8·360
	17·8	0·9304	8·320
Average	17·8	0·9314	8·329

Ethyl Ethylideneacetoacetate.

The specimen of this substance examined boiled at 112° at 15 mm. (Claisen).

The density determinations gave—

d 4°/4°	1·1082.	*d* 15°/15°	1·0986.
d 10°/10°	1·1027.	*d* 20°/20°	1·0950.
d 25°/25°	1·0914.		

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
19·6°	1·1096	9·361
19·6	1·1136	9·394
19·6	1·1077	9·345
19·6	1·1122	9·382
19·6	1·1103	9·367
Average 19·6	1·1107	9·370

Levulinic Acid.

The crystallised acid was rapidly distilled and collected in two fractions.

Fraction I.—This boiled at 249·5—251·5° (corr.) and was examined in a state of surfusion.

The density determinations gave—

d 4°/4°	1·1524.	d 15°/15°	1·1421.
d 10°/10°	1·1462.	d 20°/20°	1·1386.
d 25°/25°	1·1358.		

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
13·7°	0·9802	5·526
13·6	0·9817	5·534
13·6	0·9842	5·549
13·7	0·9802	5·526
15·3	0·9815	5·540
15·2	0·9856	5·563
15·2	0·9874	5·574
15·2	0·9867	5·569
15·3	0·9830	5·548
Average 14·5	0·9834	5·548

Fraction II.—This boiled at 251—253° corr.

The density determinations gave—

d 4°/4°	1·1537.	d 15°/15°	1·1438.
d 10°/10°	1·1478.	d 20°/20°	1·1404.
d 25°/25°	1·1376.		

The magnetic rotations gave—

	t.	Sp. rotation.	Mol. rotation.
	16°	0·9718	5·479
	16	0·9740	5·491
	16	0·9788	5·518
	16	0·9822	5·537
	16	0·9792	5·521
Average	16	0·9772	5·509

Levulinic Acid + $2H_2O$.

This solution was made with the acid of Fraction I.

The density determinations gave—

d 15°/15° 1·1228.	*d* 20°/20° 1·1197.

The magnetic rotations gave—

	t.	Sp. rotation.	Mol. rotation.
	14·2°	0·9973	7·497
	14·2	0·9981	7·503
	14·2	1·0037	7·545
	14·2	0·9939	7·471
Average	14·2	0·9983	7·504
Less 2 mols. OH_2			2
			5·504

The numbers obtained from the determination of the fused acid and the solution in water being very similar, the average of the three results may be taken, namely, 5·520, as the molecular rotation of this acid.

Ethyl Acetonedicarboxylate.

Professor v. Pechmann was kind enough to furnish me with a very pure specimen of this substance. Its boiling point was 165° at 38 mm. (Pechmann).

The density determinations gave—

d 4°/4° 1·1269.	*d* 30°/30° 1·1046.
d 10°/10° 1·1209.	*d* 35°/35° 1·1023.
d 15°/15° 1·1165.	*d* 40°/40° 1·0993.
d 20°/20° 1·1126.	*d* 45°/45° 1·0963.
d 25°/25° 1·1090.	*d* 50°/50° 1·0934

d 55°/55° 1·0908.
d 60°/60° 1·0885
d 65°/65° 1·0863.
d 70°/70° 1·0841.
d 75°/75° 1·0821.
d 80°/80° 1·0801.
d 85°/85° 1·0783.
d 90°/90° 1·0767.
d 95°/95° 1·0753.
d 100°/100° 1·0740.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
13·2°	0·9598	9·633
13·2	0·9598	9·633
13·2	0·9613	9·648
13·5	0·9604	9·641
14·2	0·9571	9·622
19·7	0·9493	9·574
19·7	0·9505	9·586
19·7	0·9479	9·559
19·7	0·9493	9·574
Average 16·2	0·9550	9·608

t.	Sp. rotation.	Mol. rotation.
94°	0·8949	9·337
94	0·9003	9·393
94	0·8967	9·356
94	0·8987	9·377
94	0·9018	9·409
Average 94	0·8985	9·374

Acetylacetone, Methylacetylacetone, and Ethylacetylacetone.

Acetylacetone, Specimen I.

The first specimen of this substance examined was prepared by Professor Dunstan and Mr. T. S. Dymond for their interesting experiments on the synthesis of trimethylisoxazole* (Trans., 1891, **59**,

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* Dunstan and Dymond, in their paper "On the Action of Alkalis on the Nitro-compounds of the Paraffin Series" (Trans., 1891, **59**, 415), have misunderstood my remarks on the magnetic rotation of trimethylisoxazole. They state that the results might "indicate that the compound is unsaturated to the extent of four equivalents of hydrogen (H_4)." The rotation of this substance is peculiar; it is too high for a saturated compound, and at the same time is scarcely high enough for a body unsaturated to the extent of H_2, and consequently agrees best with the formula they propose, which requires it to be unsaturated to this extent only.

428). It was made by Claisen's method (*Ber.*, **22**, 1010), and purified by conversion into its copper derivative, from which it was afterwards liberated by means of dilute sulphuric acid. This was examined both last year and also this year, and it will be seen that the results on both occasions were practically the same, showing that it does not change to any appreciable extent on keeping, though there is a slight difference in the densities taken on the two occasions.

Examined 1891. The boiling point of the product was 137—140° (D. and D.).

The density determinations gave—

d 4°/4°	0·9897.	*d* 15°/15°	0·9792.
d 10°/10°	0·9838.	*d* 20°/20°	0·9750.
d 25°/25°	0·9712.		

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
15·0°	1·2502	7·092
15·5	1·2590	7·146
15·5	1·2658	7·184
15·5	1·2583	7·142
15·5	1·2524	7·108
15·5	1·2539	7·116
16·0	1·2553	7·127
Average 15·5	1·2564	7·131

Examined 1892.

The density determinations gave—

d 4°/4°	0·9925.	*d* 55°/55°	0·9560.
d 10°/10°	0·9863.	*d* 60°/60°	0·9533.
d 15°/15°	0·9819.	*d* 65°/65°	0·9506.
d 20°/20°	0·9781.	*d* 70°/70°	0·9481.
d 25°/25°	0·9745.	*d* 75°/75°	0·9457.
d 30°/30°	0·9709.	*d* 80°/80°	0·9434.
d 35°/35°	0·9676.	*d* 85°/85°	0·9413.
d 40°/40°	0·9645.	*d* 90°/90°	0·9394.
d 45°/45°	0·9615.	*d* 95°/95°	0·9376.
d 50°/50°	0·9587.	*d* 100°/100°	0·9359.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
15·4°	1·2589	7·125
15·4	1·2585	7·122
15·4	1·2580	7·120
15·4	1·2580	7·120
15·7	1·2595	7·129
15·6	1·2602	7·133
15·7	1·2642	7·156
15·6	1·2605	7·135
Average 15·2	1·2597	7·130

The rotation was also determined at a higher temperature, and gave the following result:—

t.	Sp. rotation.	Mol. rotation.
85·7°	1·1131	6·571
85·7	1·1158	6·587
85·7	1·1182	6·601
85·7	1·1135	6·574
Average 85·7	1·1151	6·583

These numbers show a remarkable reduction in the rotation when determined at higher temperatures.

Methylacetylacetone, Specimen I.

This was prepared by Professor Dunstan and Mr. Dymond by heating the sodium compound of acetylacetone with methyl iodide at 140°. It was purified by fractional distillation. The boiling point of this specimen was 168·5—169° (D. and D.).

The density determinations gave—

d 4°/4°	0·9920.	*d* 15°/15°	0·9824.
d 10°/10°	0·9865.	*d* 20°/20°	0·9787.
d 25°/25°	0·9753.		

The magnetic rotations gave—

	t.	Sp. rotation.	Mol. rotation.
	15·5°	1·1306	7·291
	15·5	1·1262	7·263
	15·5	1·1262	7·263
	15·5	1·1292	7·282
	15·5	1·1226	7·240
	15·5	1·1268	7·266
	15·5	1·1216	7·233
Average	15·5	1·1261	7·263

As this substance was kept a long time before the following determinations were made, and had become yellow, evidently owing to some slight decomposition, it was redistilled, and the fraction boiling at 170—172·5° (corr.) taken for examination.

The density determinations gave—

d 4°/4°	0·9925.	*d* 55°/55°	0·9596.
d 10°/10°	0·9878.	*d* 60°/60°	0·9570.
d 15°/15°	0·9837.	*d* 65°/65°	0·9544.
d 20°/20°	0·9801.	*d* 70°/70°	0·9518.
d 25°/25°	0·9768.	*d* 75°/75°	0·9494.
d 30°/30°	0·9736.	*d* 80°/80°	0·9472.
d 35°/35°	0·9707.	*d* 85°/85°	0·9451.
d 40°/40°	0·9678.	*d* 90°/90°	0·9434.
d 45°/45°	0·9651.	*d* 95°/95°	0·9419.
d 50°/50°	0·9623.	*d* 100°/100°	0·9405.

The magnetic rotations gave—

	t.	Sp. rotation.	Mol. rotation.
	92°	0·9976	6·701
	92	0·9961	6·691
	92	0·9930	6·670
	92	0·9930	6·670
	92	0·9891	6·644
Average	92	0·9937	6·675

Two or three hours after these determinations were made, and the substance having cooled down, it was remeasured and gave the following results :—

t.	Sp. rotation.	Mol. rotation.
15·2°	1·0488	6·752
15·2	1·0488	6·752
15·2	1·0525	6·776
15·2	1·0503	6·762
15·2	1·0532	6·781
Average 15·2	1·0507	6·765

From these it is seen that the rotation is much smaller than when previously examined at about this temperature, but, on re-examination a few weeks afterwards, it was found to have regained its normal rotation. From this it is evident that the substance undergoes a considerable amount of change on heating, and does not at once regain its original character on cooling, but requires time to do so. The density of the product also becomes lower after it is heated, and this does not rise to the normal for some time. To get an idea of the rate of change of density, an experiment was made in a dilatometer, the particulars of which are given in the earlier part of this paper (p. 817).

After obtaining these remarkable results, it was thought that it would be interesting to examine a different specimen of this substance, and also of acetylacetone, and Professor Claisen very kindly prepared them for me with great care; he also furnished me with a specimen of ethylacetylacetone.

The following results were obtained with these new specimens:—

Acetylacetone, Specimen II.

This boiled at 138—138·5°, and was nearly colourless. The density determinations gave—

d 4°/4°	0·9897.	*d* 55°/55°	0·9517.
d 10°/10°	0·9837.	*d* 60°/60°	0·9492.
d 15°/15°	0·9791.	*d* 65°/65°	0·9468.
d 20°/20°	0·9748.	*d* 70°/70°	0·9445.
d 25°/25°	0·9710.	*d* 75°/75°	0·9425.
d 30°/30°	0·9674.	*d* 80°/80°	0·9404.
d 35°/35°	0·9639.	*d* 85°/85°	0·9385.
d 40°/40°	0·9606.	*d* 90°/90°	0·9366.
d 45°/45°	0·9574.	*d* 95°/95°	0·9348.
d 50°/50°	0·9545.	*d* 100°/100°	0·9334.

These are nearly identical with those obtained from specimen I, examined in 1891.

The magnetic rotations gave—

TABLE I.

	t.	Sp. rotation.	Mol. rotation.
	19·5°	1·2623	7·191
	19·5	1·2643	7·202
	19·5	1·2643	7·202
	19·5	1·2638	7·200
Average	19·5	1·2637	7·199

As it had been found that methylacetylacetone when heated does not at once regain its ordinary condition, it was thought that it would be interesting to see whether long cooling would influence this substance; it was therefore kept in ice for seven days. As it was not possible to measure its rotation at 0° in warm weather on account of dew forming on the glass ends of the measuring tubes, the substance was rapidly brought to the atmospheric temperature and quickly measured. It then gave the following results:—

TABLE II.

	t.	Sp. rotation.	Mol. rotation.
	17°	1·2746	7·246
	17	1·2725	7·234
	17	1·2731	7·238
Average	17	1·2734	7·239

Determinations were then made at higher temperatures, and gave—

TABLE III.

	t.	Sp. rotation.	Mol. rotation.
	93°	1·1182	6·640
	93	1·1213	6·658
	93	1·1186	6·642
	93	1·1182	6·639
	93	1·1209	6·656
Average	93	1·1194	6·647

The following were obtained with some of this substance which had been boiled and cooled to 100° directly before measurement:—

TABLE IV.

	t.	Sp. rotation.	Mol. rotation.
	100·2°	1·1040	6·571
	100·2	1·1022	6·560
	100·2	1·1037	6·569
	100·2	1·1045	6·573
Average	100·2	1·1036	6·568

It will be seen that the cooled specimen, Table II, gave only slightly higher results than the specimen which was examined under ordinary conditions. The boiled specimen cooled to 100°, Table IV, also gave only slightly lower results than the unboiled, if difference of temperature be considered. This might be expected from the densities of the product cooled and heated in these different ways, which gave normal results.

The examination of both specimens of acetylacetone gave practically the same rotations, as the following comparisons will show:—

t.	Spec. I.	t.	Spec. II.
15·5°	7·131 (1891)	19·5°	7·199
15·2	7·130 (1892)	17·0	7·239 (cooled in ice)
85·7	6·583	93·0	6·647
—	—	100·2	6·568 (boiled and cooled to 100°)

The average of the low temperature results is t 16·7°, mol. rot. 7·175; and for the high temperature t 93°, mol. rot. 6·599, making a difference between them of 0·576 for 76·3°, or 0·755 for 100°.

The refractive and dispersive power of this substance was determined at temperatures wide apart with specimen I with the following results (see p. 847).

Dr. Gladstone was good enough to examine specimen II, obtained from Professor Claisen; the following are his results:—

Line.	t.	μ.	$\frac{\mu - 1}{d}p$.
A........	18·4°	1·4447	45·62
F........	18·4	1·4678	47·49
H........	18·4	1·4943	50·70

Dispersion H—A = 5·08.

$d\ 11°/4°$ 0·98506. $d\ 99·3°/4°$ 0·89787.

Line.	μ.			$\frac{\mu - 1}{d}$.			$\frac{\mu - 1}{d}p$.		
	t.		Diff. for 88·3°.	t.		Diff. for 88·3°.	t.		Diff. for 88·3°.
	11°.	99·3°.		11°.	99·3°.		11°.	99·3°.	
A.............	1·444932	1·396344	0·048588	0·451680	0·441427	0·010253	45·168	44·143	1·025
C.............	1·450067	1·400321	0·049746	0·456893	0·445856	0·011037	45·689	44·586	1·103
D.............	1·454957	1·404135	0·050462	0·461492	0·450104	0·011388	46·149	45·010	1·139
F.............	1·467571	1·414139	0·053432	0·474662	0·461246	0·013416	47·466	46·125	1·341
G.............	1·479223	1·423518	0·056405	0·487201	0·471692	0·015509	48·720	47·169	1·551

Dispersion G—A = 3·552 at 11°.
" " = 3·026 " 99·3°.

Specimen II gives slightly higher results than specimen I, but the difference is but small.

The large difference obtained at temperatures 88·3° apart is consistent with the rotations, and it will be observed that a considerable decrease in the dispersion also takes place at the higher temperature.

Methylacetylacetone, Specimen II.

Professor Claisen gives the following particulars of the preparation of this specimen:—Acetylacetone was first converted into the potassium salt by dissolving it in ether and precipitating it with a solution of potash in methyl alcohol. This salt was dried, dissolved in methyl alcohol, and boiled some hours with methyl iodide until the mixture was neutral to test paper. Ether was then added, and the liquid filtered from potassium iodide, and, after evaporating the ether, the product was distilled under reduced pressure (about 20 mm.). It was further purified by dissolving it in ether, and precipitating with potash in methyl alcohol, and the potassium derivative, $CH_3{\cdot}CO{\cdot}CK(CH_3){\cdot}CO{\cdot}CH_3$, thus obtained, was well washed with ether, and dried. It was then dissolved in water, decomposed with dilute sulphuric acid, and the product distilled three times under reduced pressure; all came over between 74° and 75° under a pressure of 20 mm. This was the highest temperature this specimen of methylacetylacetone was subjected to in its preparation.

The density determinations gave—

d 4°/4°	0·9941.	*d* 10°/10°	0·9887.
d 15°/15°	0·9845.	*d* 20°/20°	0·9808.
d 25°/25°	0·9773.	*d* 100°/100°	0·9408.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
19·2°	1·1286	7·284
19·2	1·1330	7·312
19 2	1·1330	7·312
19·2	1·1345	7·322
19·2	1·1308	7·298
Average 19·2	1·1320	7·306

After being kept in ice for seven days,
The density determinations gave—

d 4°/4°	0·9964.	*d* 15°/15°	0·9866.

The magnetic rotations gave—

	t.	Sp. rotation.	Mol. rotation.
	17·5°	1·1360	7·306
	17·5	1·1319	7·279
	17·5	1·1368	7·310
	17·5	1·1363	7·308
Average	17·5	1·1352	7·301

Determination at a Higher Temperature.

The magnetic rotations gave—

	t.	Sp. rotation.	Mol. rotation.
	100·7°	0·9934	6·689
	100·7	0·9872	6·647
	100·7	0·9919	6·678
	100·7	0·9872	6·647
Average	100·7	0·9899	6·665

It was thought that probably the specimen cooled in ice would have given rather higher numbers than that which had been kept at the atmospheric temperature, but although the density is a trifle higher, the molecular rotation has come out practically the same.

The following is a comparison of the molecular rotations obtained from the two different specimens of methylacetylacetone.

t.	Spec. I.	t.	Spec. II.
15·5°	7·263	19·2°	7·306
—	—	17·5	7·301
92·0	6·675	100·7	6·665

These results agree very closely, showing that both preparations behaved in the same manner.

The average rotations are—

	t.	Mol. rotation.
	17·4°	7·290
	96·4	6·670
Difference ..	79·0	0·620

The difference for 100° would be 0·785, or a trifle more than that found for acetylacetone.

d 8·34°/4° 0·99189. d 99·2°/4° 0·90324.

Line.	μ.			$\frac{\mu-1}{d}$.			$\frac{\mu-1}{d}p$.		
	t.		Diff. for 90·86°.	*t.*		Diff. for 90·86°.	*t.*		Diff. for 90·86°.
	8·34°.	99·2°.		38·4°.	99·2°.		8·34°.	99·2°.	
A..............	1·442103	1·395261	0·046842	0·445720	0·437603	0·008117	50·812	49·887	0·925
C..............	1·445864	1·398382	0·047482	0·449512	0·441058	0·008454	51·244	50·281	0·963
D..............	1·449414	1·401186	0·048228	0·453091	0·444163	0·008928	51·652	50·635	1·017
F..............	1·458978	1·408530	0·050448	0·462733	0·452293	0·010440	52·752	51·561	1·191

Dispersion F—A = 1·940 at 8·34°.
" " = 1·673 " 99·2°.

The determination of the refractive and dispersive powers of this substance, made with specimen I at temperatures wide apart, gave results in table, p. 850. The substance being rather yellow, the line G could not be measured.

A corresponding set of determinations was made with specimen II. This, however, had become yellow by keeping; it was therefore distilled, and the fraction boiling at 170—172° (corr.) taken. This was kept in ice five days after distillation before it was examined (see p. 852).

These numbers are remarkably near to those obtained with specimen I, those for the higher temperature being practically identical, and those for the lower only differing on an average by + 0·155, probably due to the product having been kept at a low temperature before examination, and the presence consequently of a slightly larger proportion to the hydroxylic compound.

As in the case of acetylacetone, large differences are seen to exist at temperatures wide apart, and also a considerable decrease in the dispersion is observable at the higher temperatures. These results are consistent with the magnetic rotation.

Ethylacetylacetone.

This substance boiled at 180—184° (Claisen).

The density determinations gave—

d 4°/4°	0·9711.	*d* 55°/55°	0·9382.
d 10°/10°	0·9660.	*d* 60°/60°	0·9359.
d 15°/15°	0·9620.	*d* 65°/65°	0·9338.
d 20°/20°	0·9584.	*d* 70°/70°	0·9317.
d 25°/25°	0·9541.	*d* 75°/75°	0·9295.
d 30°/30°	0·9519.	*d* 80°/80°	0·9275.
d 35°/35°	0·9488.	*d* 85°/85°	0·9255.
d 40°/40°	0·9460.	*d* 90°/90°	0·9238.
d 45°/45°	0·9433.	*d* 95°/95°	0·9223.
d 50°/50°	0·9407.	*d* 100°/100°	0·9208.

The magnetic rotations gave—

	t.	Sp. rotation.	Mol. rotation.
	18·8°	1·0589	7·850
	18·8	1·0645	7·891
	18·8	1·0616	7·869
	18·8	1·0726	7·952
	18·8	1·0645	7·891
Average	18·8	1·0644	7·890

d 15·4°/4° 0·98570. d 100·3°/4° 0·90521.

Line.	μ.			$\frac{\mu - 1}{d}$.			$\frac{\mu - 1}{d}p$.		
	t.		Diff. for 84·9°.	t.		Diff. for 84·9°.	t.		Diff. for 84·9°.
	15·4°.	100·3°.		15·4°.	100·3°.		15·4°.	100·3°.	
A.............	1·440659	1·395214	0·045445	0·447052	0·437605	0·009447	50·964	49·887	1·077
C.............	1·444430	1·398348	0·046082	0·450878	0·441075	0·009803	51·400	50·283	1·117
D.............	1·448198	1·401151	0·047047	0·454700	0·444179	0·010521	51·836	50·641	1·195
F.............	1·458283	1·408612	0·049671	0·463863	0·452440	0·011423	52·880	51·578	1·302

Dispersion F—A = 1·916 at 15·4°.
" " = 1·691 at 100·3°.

t.	Sp. rotation.	Mol. rotation.
92·9°	0·9840	7·582
92·9	0·9806	7·556
92·9	0·9794	7·547
92·9	0·9791	7·544
92·9	0·9840	7·582
Average 92·9	0·9814	7·562

The difference between the rotations of this substance at the temperatures employed is 0·328 for 74·1° or 0·443 for 100°, which is only a little more than half that obtained in the case of acetylacetone and methylacetylacetone, the larger radicle evidently having a retarding influence in this respect.

Methyl Acetoneoxalate.

This substance melts at 63—64° (Claisen), and had, therefore, to be examined in a fused condition.

The density determinations gave—

d 60°/60°	1·1589.	*d* 80°/80°	1·1489.
d 65°/65°	1·1562.	*d* 85°/85°	1·1467.
d 70°/70°	1·1536.	*d* 90°/90°	1·1450.
d 75°/75°	1·1512.	*d* 95°/95°	1·1439.

d 100°/100° 1·1432.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
66°	1·2829	8·880
66	1·2826	8·878
66	1·2882	8·917
66	1·2897	8·927
66	1·2791	8·846
66	1·2728	8·810
Average 66	1·2825	8·876

Ethyl Acetoneoxalate.

The boiling point of this specimen was 113—116° under 19 mm. (Claisen).

The density determinations gave—

d 15°/15°	1·1318.	d 60°/60°	1·1026.
d 20°/20°	1·1277.	d 65°/65°	1·1000.
d 25°/25°	1·1239.	d 70°/70°	1·0976.
d 30°/30°	1·1203.	d 75°/75°	1·0952.
d 35°/35°	1·1169.	d 80°/80°	1·0928.
d 40°/40°	1·1137.	d 85°/85°	1·0906.
d 45°/45°	1·1107.	d 90°/90°	1·0888.
d 50°/50°	1·1079.	d 95°/95°	1·0872.
d 55°/55°	1·1052.	d 100°/100°	1·0860.

The magnetic rotations gave—

	t.	Sp. rotation.	Mol. rotation.
	19·8°	1·2995	10·111
	19·7	1·2995	10·111
	19·7	1·2980	10·100
	19·7	1·3035	10·143
	19·7	1·3013	10·125
	20·2	1·2991	10·112
	20·2	1·3067	10·172
	20·2	1·3027	10·140
Average	20·0	1·3013	10·127

	t.	Sp. rotation.	Mol. rotation.
	89·5°	1·2197	9·829
	89 5	1·2182	9·818
	89·5	1·2167	9·805
	89·5	1·2197	9·829
	89·5	1·2182	9·818
Average	89·5	1·2185	9·820

The refraction determinations gave the results in table, p. 855.

Dr. Gladstone also determined the refractive power of this substance, and obtained—

Line.	t.	μ.	$\frac{\mu - 1}{d}p$.
A	22·1°	1·4643	65·28
F	22·1°	1·4892	68·78
H	22·1°	1·5185	72·89

Dispersion H—A = 7·61 at 22·1°.

Ethyl Diacetoacetate.

Prepared by the action of acetyl chloride on ethyl sodacetoacetate. Its boiling point was 103—105° at 19 mm. (Claisen).

d 17°/4° 1·12879. d 100°/4° 1·04109.

Line.	μ.			$\frac{\mu - 1}{d}$.			$\frac{\mu - 1}{d}p$.		
	t.		Diff. for 83°.	t.		Diff. for 83°.	t.		Diff. for 83°.
	17°.	100°.		17°.	100°.		17°.	100°.	
A	1·465028	1·426166	0·038862	0·411970	0·409344	0·002626	65·091	64·676	0·415
C	1·470244	1·430845	0·039399	0·416591	0·413838	0·002753	65·821	65·386	0·435
D	1·475699	1·435508	0·040191	0·421424	0·418317	0·003107	66·585	66·094	0·491
F	1·490047	1·448699	0·041348	0·434135	0·430988	0·003147	68·593	68·096	0·497

Dispersion F—A = 3·502 at 17°.
„ „ = 3·420 „ 100°.

The density determinations gave—

d 4°/4°	1·1073.	d 55°/55°	1·0696.
d 10°/10°	1·1012.	d 60°/60°	1·0670.
d 15°/15°	1·0967.	d 65°/65°	1·0646.
d 20°/20°	1·0950.	d 70°/70°	1·0622.
d 25°/25°	1·0889.	d 75°/75°	1·0598.
d 30/°30°	1·0854.	d 80°/80°	1·0575.
d 35°/35°	1·0819.	d 85°/85°	1·0553.
d 40°/40°	1·0786.	d 90°/90°	1·0534.
d 45°/45°	1·0754.	d 95°/95°	1·0516.
d 50°/50°	1·0724.	d 100°/100°	1·0499.

The magnetic rotations gave—

	t.	Sp. rotation.	Mol. rotation.
	19·8°	1·2202	10·670
	19·8	1·2217	10·683
	19·8	1·2179	10·651
	19·8	1·2214	10·681
	19·8	1·2243	10·707
Average	19·8	1·2211	10·678

After being in ice for seven days,

	t.	Sp. rotation.	Mol. rotation.
	17°	1·2275	10·717
	17	1·2290	10·730
	17	1·2275	10·717
Average	17	1·2280	10·721

Average of above, 10·699 at 18·4°.

The magnetic rotations gave—

	t.	Sp. rotation.	Mol. rotation.
	92·6°	1·1499	10·441
	92·6	1·1510	10·451
	92·6	1·1507	10·448
	92·6	1·1518	10·458
Average	92·6	1·1508	10·449

The refraction determinations gave—

d 17·6°/4° 1·09313. d 99·8°/4° 1·0675.

Line.	μ.			$\frac{\mu - 1}{d}$.			$\frac{\mu - 1}{d}p$.		
	t.		Diff. for 82·2°.	t.		Diff. for 82·2°.	t.		Diff. for 82·2°.
	17·6°.	99·8°.		17·6°.	99·8°.		17·6°.	99·8°.	
A.............	1·457287	1·419323	0·037964	0·418328	0·416520	0·001808	71·952	71·641	0·311
C.............	1·461759	1·423412	0·038347	0·422419	0·420582	0·001837	72·656	72·340	0·316
D.............	1·466017	1·427286	0·038731	0·426315	0·424429	0·001886	73·326	73·002	0·324
F.............	1·476844	1·437025	0·039819	0·436219	0·434104	0·002115	75·030	74·666	0·364
G.............	1·487186	1·446191	0·040995	0·445680	0·443208	0·002472	76·657	76·232	0·425

Dispersion G—A = 4·705 at 17·6°.
" " = 4·591 " 99·8°.

Dr. Gladstone has likewise examined this substance, and obtained the following result:—

Line.	$t.$	$\mu.$	$\frac{\mu - 1}{d}p.$
A	22·8°	1·4549	71·91
F	22·8°	1·4761	75·27
H	22·8°	1·4975	78·65

Dispersion H—A = 6·74 at 22·8°.

Diacetylacetone.

Dr. Collie very kindly prepared the specimen of this substance for me from dehydracetic acid; when fused, it becomes coloured slightly red, and this rendered the readings for the magnetic rotations a little difficult.

The density determinations gave—

d 40°/40°	1·0681.	*d* 70°/70°	1·0564.
d 45°/45°	1·0660.	*d* 75°/75°	1·0547.
d 50°/50°	1·0639.	*d* 80°/80°	1·0531.
d 55°/55°	1·0620.	*d* 85°/85°	1·0515.
d 60°/60°	1·0601.	*d* 90°/90°	1·0504.
d 65°/65°	1·0583.	*d* 95°/95°	1·0497.
d 100°/100°	1·0494.		

The magnetic rotations gave—

$t.$	Sp. rotation.	Mol. rotation.
56·0°	1·3870	10·307
56·0	1·3837	10·282
56·0	1·3780	10·240
56·0	1·3779	10·240
56·0	1·3930	10·352
57·5	1·3913	10·345
57·5	1·3937	10·363
57·5	1·3811	10·269
57·5	1·3762	10·233
64·2	1·3530	10·084
64·2	1·3533	10·086
64·2	1·3472	10·041
64·2	1·3499	10·061
Average 59·0	1·3742	10·223

t.	Sp. rotation.	Mol. rotation.
92·75°	1·2730	9·565
96·0	1·2826	9·637
97·5	1·2716	9·555
99·0	1·2764	9·591
Average 96·3	1·2759	7·587

The difference in the rotation of this and the previous amounts to 0·635 for 37·3°, or 1·704 for 100°.

The refraction determinations gave results in table, p. 860.

Ethyl β-Amidocrotonate.

This was examined at two temperatures; for the first it was used in a state of surfusion.

The density determinations gave—

d 15°/15°	1·0273.	*d* 60°/60°	1·0034.
d 20°/20°	1·0239.	*d* 65°/65°	1·0015.
d 25°/25°	1·0207.	*d* 70°/70°	0·9997.
d 30°/30°	1·0178.	*d* 75°/75°	0·9981.
d 35°/35°	1·0150.	*d* 80°/80°	0·9965.
d 40°/40°	1·0124.	*d* 85°/85°	0·9950.
d 45°/45°	1·0099.	*d* 90°/90°	0·9937.
d 50°/50°	1·0076.	*d* 95°/95°	0·9925.
d 55°/55°	1·0054.	*d* 100°/100°	0·9913.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
15·0°	1·5467	10·790
15·0	1·5482	10·800
15·2	1·5455	10·782
15·2	1·5381	10·732
15·2	1·5452	10·780
15·2	1·5425	10·761
15·2	1·5474	10·795
16·2	1·5437	10·778
17·4	1·5430	10·781
19·0	1·5370	10·750
Average 15·8	1·5437	10·775

d 6°/4° 1·04248. d 99·8°/4° 1·00615.

Line.	μ.			$\frac{\mu - 1}{d}$.			$\frac{\mu - 1}{d}p$.		
	t.		Diff. for 39·8°.	t.		Diff. for 39·8°	t.		Diff. for 39·8°.
	60°.	99·8°.		60°.	99·8°.		60°.	99·8°.	
A..............	1·466906	1·443863	0·023043	0·447880	0·441148	0·006732	63·599	62·643	0·956
C..............	1·472819	1·449500	0·023319	0·453551	0·446750	0·006801	64·404	63·439	0·965
D..............	1·478704	1·454498	0·024206	0·459197	0·451715	0·007482	65·206	64·143	1·063
F..............	1·495610	1·468927	0·026683	0·475414	0·466059	0·009355	67·509	66·180	1·329

As it became slightly red in colour the line G could not be measured.

Dispersion F—A = 3·919 at 60°.
" " = 3·537 " 99·8°.

t.	Sp. rotation.	Mol. rotation.
86·5°	1·4508	10·454
86·5	1·4631	10·543
86·5	1·4573	10·500
86·5	1·4536	10·498
86·5	1·4542	10·478
Average 86·5	1·4558	10·494

The determination of its refractive and dispersive powers gave—

$d\,16°/4°$ 1·02578. $d\,15·8°/4°$ 1·02551.

Line.	t.	μ.	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d}p$.
A................	16°	1·49032	0·47805	61·668
C................	16	1·49633	0·48390	62·423
D................	16	1·50209	0·48952	63·148
F................	16	1·51806	0·50509	65·157
G................	16	1·53334	0·51998	67·078

Dispersion G—A = 5·410 at 16°.

A second set of determinations were made with this product after it had been allowed to crystallise, and was thoroughly pressed between bibulous paper, to remove any traces of oily products which had been produced by the action of heat.

Line.	t.	μ.	$\frac{\mu - 1}{d}$.	$\frac{\mu - 1}{d}p$.
A................	15·8°	1·49131	0·47908	61·802
C................	15·8	1·49672	0·48436	62·482
D................	15·8	1·50273	0·49022	63·239
F................	15·8	1·51863	0·50573	65·239
G................	15·8	1·53403	0·52075	67·176

Dispersion G—A = 5·374 at 15·8°.

Ethyl Benzoylacetate.

The specimen examined was obtained from Kahlbaum.

The density determinations gave—

d 4°/4°	1·1311.	*d* 55°/55°	1·1008.
d 10°/10°	1·1259.	*d* 60°/60°	1·0990.
d 15°/15°	1·1219.	*d* 65°/65°	1·0973.
d 20°/20°	1·1186.	*d* 70°/70°	1·0957.
d 25°/25°	1·1154.	*d* 75°/75°	1·0943.
d 30°/30°	1·1126.	*d* 80°/80°	1·0930.
d 35°/35°	1·1099.	*d* 85°/85°	1·0919.
d 40°/40°	1·1073.	*d* 90°/90°	1·0910.
d 45°/45°	1·1050.	*d* 95°/95°	1·0903.
d 50°/50°	1·1029.	*d* 100°/100°	1·0896.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
17·5°	1·7224	16·402
17·5	1·7182	16·362
17·5	1·7220	16·398
17·5	1·7242	16·419
20·5	1·7136	16·347
20·5	1·7188	16·397
20·5	1·7217	16·425
Average 18·8	1·7201	16·393

t.	Sp. rotation.	Mol. rotation.
99·0°	1·6285	15·941
99·7	1·6251	15·909
100·7	1·6273	15·930
100·7	1·6229	15·887
100·7	1·6207	15·867
100·7	1·6253	15·913
Average 100·6	1·6249	15·908

As the influence of heat on the rotation of stable aromatic compounds is much greater than on those of the fatty series, it is necessary to allow for this before considering what the influence of temperature is on the chemical constitution of the substance. In this instance it will probably be most accurate to take the average of the difference found for a ketone and carboxylic acid, thus:—

Influence of heat on the rotation of acetophenone per 100° = 0·298
Influence of heat on the rotation of ethereal salt
of an aromatic carboxylic acid .... ,, = 0·399

Average .... ,, 0·348

Therefore, on the above rotation, 81·8° above the preceding one, this will be 0·284. The rotation will then be

$$15·908 + 0·284 = 16·192.$$

Benzoylacetone.

Dr. Claisen purified this substance by precipitating it from its alkaline solution with carbonic acid. It melted at 58°, and was examined in the fused state.

The density determinations gave—

d 60°/60° 1·0899.
d 65°/65° 1·0862.
d 70°/70° 1·0898.
d 75°/75° 1·0834.
d 80°/80° 1·0823.
d 85°/85° 1·0812.
d 90°/90° 1·0805.
d 95°/95° 1·0801.
d 100°/100° 1·0800.

As this substance was slightly brownish when fused, and became more so when kept in this condition, it was found impossible to measure it in a tube of the length usually employed (102 mm.); one of about half that length was therefore used, but even in this the colour obstructed the passage of the light to a very large extent, and made the readings difficult.

The magnetic rotations gave—

t.	Sp. rotation.	Mol. rotation.
61·0°	2·2673	18·762
63·0	2·2688	18·787
64·0	2·2749	18·824
64·0	2·2662	18·773
64·0	2·2651	18·763
Average 63·2	2·2684	18·782

Methyl Acetophenoneoxalate.

This substance was examined in the fused state; it melts at 61°.

The density determinations gave—

d 65°/65° 1·1574.
d 70°,70° 1·1551.
d 75°/75° 1·1528.
d 80°/80° 1·1504.
d 85°/85° 1·1481.

The remarks made in reference to benxoylacetone also apply to this substance, but, besides, the colour obstructing the light, there was a slight opalescence which could not be got rid of by filtering the fused substance, and it was only with great difficulty readings could be obtained in a tube half the ordinary length. The results were, therefore, rather rough, but the averages given, being obtained from 64 readings, are probably not far from the truth; they are:—

t.	Sp. rotation.	Mol. rotation.
66·5°	2·1739	21·511

Ethyl Acetophenoneoxalate.

The melting point of this substance was 42° (Claisen).

The density determinations gave—

d 20°/20°	1·1867.	*d* 60°/60°	1·1674.
d 25°/25°	1·1839.	*d* 65°/65°	1·1657.
d 30°/30°	1·1811.	*d* 70°/70°	1·1641.
d 35°/35°	1·1784.	*d* 75°/75°	1·1625.
d 40°/40°	1·1758.	*d* 80°/80°	1·1611.
d 45°/45°	1·1734.	*d* 85°/85°	1·1600.
d 50°/50°	1·1702.	*d* 90°/90°	1·1592.
d 55°/55°	1·1682.	*d* 95°/95°	1·1589.
		d 100°/100°	1·1588.

The magnetic rotation gave—

	t.	Sp. rotation.	Mol. rotation.
	47·3°	2·1254	22·152
	49·5	2·1207	22·124
	48·3	2·1300	22·212
	47·1	2·1255	22·158
	45·5	2·1266	22·154
Average	47·5	2·1256	22·160

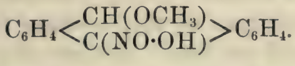
This substance, when melted, was of a yellowish colour, and was measured in an ordinary tube of 102 mm. in length; it was, however, very slightly cloudy, and could not be rendered quite clear by filtration, this cloudiness was evidently due to the presence of a trace of some crystalline substance, as it interfered with the polarised light, and thus impaired the sensitiveness of the observations; to overcome as much as possible the errors which might arise from this source, a very large number of observations were made, and each of the five series given above are averages of about 20 (making in all 100), whereas, in most cases, they are averages of 8 or 10 only.

LXXIV.—CONTRIBUTIONS FROM THE LABORATORIES OF THE HERIOT WATT COLLEGE, EDINBURGH.

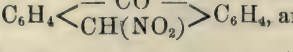
Action of Nitric Acid upon Anthracene. Part II.

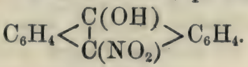
By A. G. PERKIN and J. E. MACKENZIE, B.Sc.

IN a previous communication to the Society (Trans., 1891, **59**, 634), an account was given by one of us of the action of nitric acid upon anthracene in the presence of ethyl and methyl alcohols. The substances thus obtained were found to be addition products of methyl and ethyl nitrates to anthracene, the formula of the former substance being $C_{14}H_{10},CH_3\cdot NO_3$, and its constitution being probably represented thus:—



$$C_6H_4<\begin{matrix}CH(OCH_3)\\C(NO\cdot OH)\end{matrix}>C_6H_4.$$

In studying this subject further, it occurred to us that it would be a matter of interest to determine whether this reaction is a general one, and as the result of our experiments with various alcohols, we have found that in the case of propyl, isobutyl, and benzyl alcohols compounds with anthracene similar to those already described are obtained, whereas in the case of trimethylcarbinol, no such compound could be isolated, the reaction proceeding in a different manner with formation of nitrosoanthrone. As a general rule, with the alcohols already experimented with, the only products of the reaction are substances of the general formula $C_{14}H_{10},RNO_3$. In experiments with isobutyl alcohol, however, it was found that by slightly altering the conditions, a substance is formed which, on analysis, was found to have the formula $C_{14}H_9NO_3$. The investigation of the properties of this new compound leaves scarcely any doubt that its constitution is represented by the formula  $C_6H_4<\begin{matrix}—CO—\\CH(NO_2)\end{matrix}>C_6H_4$, and we therefore propose to name it *nitroanthrone.*

This substance, on treatment with alcoholic potash, is converted into the isomeric nitroanthrole,  $C_6H_4<\begin{matrix}C(OH)\\|\\C(NO_2)\end{matrix}>C_6H_4$.

The constitution of the two last-named substances was deduced from the fact that alcoholic ammonia or acids do not convert them into nitrosoanthrone, and further, that no nitronitrosoanthrone is formed from them by treatment with fuming nitric acid and nitrobenzene, showing that they contain no nitroso-group, and therefore probably have the above constitution.

Also included in this research is the action of nitric acid on mixtures of anthracene with pure acetone and ether. In the first place, a very good yield of anthracene methyl nitrate was obtained, showing that acetone, under the conditions used, must have yielded methyl nitrate. With methylated ether free from alcohol, a mixture of anthracene ethyl and methyl nitrates was obtained, the formation of the latter being accounted for by the presence of small quantities of methyl ether or methyl ethyl ether in the sample used. The formation of anthracene methyl nitrate is so readily detected, that this reaction might possibly be employed in proving the presence of a methyl group in methyl ketones and methyl ethers.

Anthracene Propyl Nitrate, $C_{14}H_{10}NO_2{\cdot}OC_3H_7$.

In order to prepare this substance, 3 c.c. of nitric acid (sp. gr. 1·5), purified by boiling with nitrate of urea, is carefully mixed with 7 c.c. of normal propyl alcohol, and to this mixture finely powdered pure anthracene is added, until the whole becomes of a creamy consistency. The mixture is very gently warmed, when the anthracene slowly dissolves, forming a thick, pale yellow solution. This, after filtration through glass wool, is mixed with its own bulk of methyl alcohol, and allowed to stand for some hours; the hard, crystalline mass which separates is collected, pressed, washed with a little methyl alcohol, recrystallised two or three times from this solvent, and dried at 60°.

0·1300 gram of substance gave 0·3421 gram CO_2 and 0·072 gram H_2O.

0·1758 gram of substance gave 7·8 c.c. N ; $t = 20°$; bar. = 748 mm.

	Theory for $C_{17}H_{17}NO_3$.	Found.
C	72·08 per cent.	72 32 per cent.
H.......	6·00 ,,	6·20 ,,
N	4·99 ,,	4·94 ,,

As thus obtained, anthracene propyl nitrate consists of beautiful, four-sided prisms, very soluble in hot methyl alcohol, acetic acid, and benzene. It melts at 92°, and decomposes at higher temperatures with evolution of nitrous fumes and formation of anthraquinone. Chromic acid in acetic acid solution oxidises it to anthraquinone. Cold concentrated sulphuric acid dissolves it, forming a deep red solution, which quickly turns black on treatment with water, and deposits a thick, black precipitate from which nothing crystalline could be isolated. It is readily decomposed by boiling with alcoholic ammonia with formation of an orange-coloured solution, and this, on cooling, deposits long, orange-coloured needles, melting at 144°, and having all the properties of nitrosoanthrone. Alcoholic potash produces a similar result, and in this respect anthracene propyl nitrate differs from the corresponding methyl and ethyl derivatives, which, by this treatment, yield nitrosoanthrone and pseudonitrosoanthrone (Trans., 1891, **59**, 645). It is readily attacked by a mixture of nitric acid (sp. gr. 1·5) and nitrobenzene, with formation at first of a clear solution, which, on adding more of the substance, deposits crystals of nitronitrosoanthrone.

Anthracene Isobutyl Nitrate, $C_{14}H_{10}NO_2 \cdot OC_4H_9$.

The method employed in preparing this substance is similar to that described in the case of the propyl compound. There is, however, as mentioned in the Introduction, a tendency to the formation of nitroanthrone in this reaction, so that the following precautions are necessary in order to obtain a good yield of anthracene isobutyl nitrate. The anthracene must be added as rapidly as possible to the mixture of acid and alcohol, the whole warmed until solution is effected, filtered through glass wool, and, after thorough cooling, the solution is treated with about twice its bulk of low boiling petroleum. After standing for a few hours, a crystalline cake is obtained, which is collected, washed with light petroleum, and crystallised from carbon bisulphide.

The analysis of the substance dried at 60° gave the following results:—

0·1323 gram of substance gave 0·3500 gram CO_2, 0·0775 gram H_2O.
0·1072 „ „ „ 0·2860 gram CO_2; H_2O lost.
0·1590 „ „ „ 6·95 c.c. N; $t = 19°$; bar. = 756 mm.

	Theory for $C_{18}H_{19}NO_3$.	Found. I.	II.	III.
C......	72 72 p. c.	72·15	72·76	— p. c.
H......	6·39 „	6·50	lost	— „
N......	4·71 „	—	—	4·99 „

This beautiful substance crystallises in large, thick, colourless prisms, which on more than one occasion were obtained over 2 inches in length.

We are indebted to Dr. H. Marshall, of Edinburgh University, for the following examination of these crystals:—

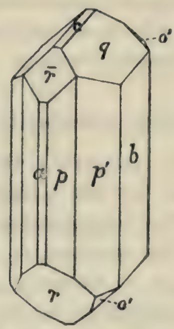
System:—Monosymmetric.

$$a : b : c = 0·8554 : 1 : 0·8563.$$

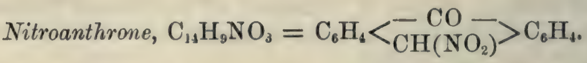
$$\beta = 74° \ 39\tfrac{1}{2}'.$$

Forms observed:—$a = \{100\}$, $b = \{010\}$, $c = \{001\}$, $p = \{110\}$, $p' = \{120\}$, $q = \{011\}$, $\bar{r} = \{101\}$, $r = \{\bar{1}01\}$, $o' = \{\bar{1}22\}$.

Figure.—Colourless, transparent prisms usually forming stellar groups, so that only one end is properly developed. They are generally long and thin, rarely short and thick. As a rule, the prism faces are much striated longitudinally. The crystals are brittle with uneven fracture, and no well-marked cleavage. Of the forms observed c, $\bar{r}$, and o' occur less frequently than the others, and often only one face of o' is present.



When heated in a capillary tube, anthracene isobutyl nitrate becomes yellow at 100°, and melts at 121° with gradual decomposition. On rapid heating, it decomposes suddenly at 165°, with evolution of nitrous fumes, a strong odour of isobutyl nitrite being noticeable. It is readily soluble in hot alcohol and acetone with slight decomposition, forming yellowish-brown solutions, and also in hot benzene and carbon bisulphide, but without decomposition. Hot alcoholic potash dissolves it easily, forming a deep red solution, which when poured into water, deposits a reddish-yellow precipitate; this, on recrystallisation, forms yellow needles melting at 144°, and having all the properties of nitrosoanthrone. The filtrate from the precipitate contains a minute trace of a phenolic substance, which, however, was too small for investigation. On oxidation with chromic acid, anthracene isobutyl nitrate yields anthraquinone, and with a mixture of nitric acid and nitrobenzene, nitronitrosoanthrone.



Nitroanthrone, $C_{14}H_9NO_3 = C_6H_4{<}\begin{matrix}-\,CO\,-\\CH(NO_2)\end{matrix}{>}C_6H_4$.

If anthracene is *very gradually* added to a mixture of nitric acid and isobutyl alcohol, anthracene isobutyl nitrate is not formed, the reaction proceeding in a different manner. In order to investigate this decomposition, the addition of anthracene was continued until it no longer dissolved, and the mixture then gently warmed, filtered through glass wool, and the filtrate treated with light petroleum. Crystals gradually separated, and at the end of 24 hours they were collected, washed with light petroleum, and purified by two or three crystallisations from carbon bisulphide or benzene.

Analyses of the colourless needles thus obtained gave the following results :—

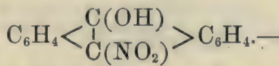
0·1107 gram of substance gave 0·2856 gram CO_2 and 0·0391 gram H_2O.

0·1946 gram of substance gave 9·6 c.c. N ; $t = 24°$; bar. $= 751$ mm.

	Theory. $C_{14}H_9NO_3$.	Found.
C.......	70·29 per cent.	70·36 per cent.
H.......	3·76 ,,	3·92 ,,
N.......	5·85 ,,	5·46 ,,

Nitroanthrone crystallises in glistening needles, which, when heated at 100°, become violet coloured, and melt at 140° with evolution of nitrous fumes and formation of anthraquinone. It is readily soluble in hot benzene and carbon bisulphide, but more sparingly in hot alcohol, with slight decomposition and formation of a pink solution which gradually becomes reddish-brown. It is readily attacked by cold sulphuric acid with total decomposition. That the formula given at the head of this section correctly represents the constitution of this substance is rendered probable from the fact that it is not converted into nitronitrosoanthrone by the action of a mixture of nitric acid and nitrobenzene. A number of experiments were instituted with a view of converting this substance into the dinitroanthrone described by Liebermann and Landshoff (*Ber.*, **14**, 472), with negative results, as anthraquinone alone was always produced.

Action of Alcoholic Potash on Nitroanthrone.

Nitroanthrole, $C_{14}H_9NO_3$ or  $C_6H_4<\begin{matrix}C(OH)\\|\\C(NO_2)\end{matrix}>C_6H_4$.—Nitroanthrone dissolves readily in alcoholic potash forming a deep orange-red solution, which, after boiling for a few minutes and diluting with water, deposits a small quantity of crystalline matter, found on examination to consist of anthraquinone.

The filtrate, on treatment with hydrochloric acid, deposits a colourless precipitate, mixed with a small quantity of a scarlet substance. The whole was extracted with ether, the ethereal solution washed well, evaporated nearly to dryness, and the greenish-coloured, crystalline mass which separated purified by crystallisation from carbon bisulphide. The resulting colourless needles gave the following results on analysis :—

0·1230 gram of substance gave 0·3185 gram CO_2 and 0·0462 gram OH_2.

0·1758 gram of substance gave 8·6 c.c. N; $t = 19°$; bar. $= 753$ mm.

	Theory for $C_{14}H_9NO_3$.	Found.
C........	70·29 per cent.	70·61 per cent.
H	3·76 ,,	4·17 ,,
N........	5·85 ,,	5·57 ,,

This substance, which we propose to name *nitroanthrole*, melts at 148° with decomposition and formation of anthraquinone. It is readily soluble in hot benzene and carbon bisulphide, but only sparingly in hot methyl alcohol, with slight decomposition and formation of a pink solution. Cold dilute alkalis dissolve it somewhat sparingly, readily on warming, with formation of orange-yellow solutions. It does not yield an acetyl derivative with acetic anhydride, but on boiling with it is decomposed with formation of anthraquinone. Anthraquinone is also formed when nitroanthrole is oxidised with chromic acid or treated with nitric acid and nitrobenzene. Nitroanthrole is isomeric with nitroanthrone, and, therefore, probably has the constitution assigned to it at the head of this section.

Action of Nitric Acid on Anthracene in the presence of Trimethylcarbinol.

3 c.c. of purified nitric acid (sp. gr. 1·5) were mixed with 7 c.c. of trimethylcarbinol, and to this mixture powdered anthracene was added. It dissolved readily at first, and the solution was afterwards completed by a gentle heat. On cooling, the whole became a nearly solid mass of yellow needles, which were purified by recrystallisation from alcohol. They melted at 144°, and had all the properties of nitrosoanthrone. Analysis :—

0·1300 gram gave 7 c.c. N; $t = 20°$; bar. $= 746$ mm.

	Theory for $C_{14}H_9NO_2$.	Found.
N	6·27 per cent.	6·04 per cent.

Numerous experiments were instituted under varied conditions with the hope of obtaining a compound of anthracene with this alcohol, similar to those already described, but in every case nitrosoanthrone was the sole product.

Anthracene Benzyl Nitrate, $C_{14}H_{10}NO_2{\cdot}OC_7H_7$.

This may be prepared in a similar manner to the analogous compounds previously described. The semi-solid, crystalline mass obtained is washed with a little methyl alcohol, pressed, and further purified by crystallisation from alcohol. Analysis gave the following results:—

0·1312 gram of substance gave 0·3669 gram CO_2 and 0·0654 gram OH_2.

0·1396 gram of substance gave 5·6 c.c. N; $t = 20°$; bar. $= 744$ mm.

	Theory for $C_{21}H_{17}NO_3$.	Found.
C........	76·13 per cent.	76·26 per cent.
H........	5·13 ,,	5·53 ,,
N........	4·23 ,,	4·49 ,,

Anthracene benzyl nitrate crystallises from alcohol in beautiful, glistening needles. It is only sparingly soluble in alcohol, but very soluble in hot carbon bisulphide and benzene. When heated, it becomes yellow at 125°, melts at 138°, and decomposes rapidly at 150°, with evolution of nitrous fumes and formation of anthraquinone. In its reactions it exactly resembles the corresponding derivatives of anthracene already described.

Action of Nitric Acid on Anthracene in the presence of Acetone and Ether respectively.

The acetone used for this experiment was Kahlbaum's pure acetone prepared from the bisulphite compound. Anthracene was added to a mixture of acetone and nitric acid, and the product crystallised from alcohol. The analysis of the beautiful, colourless, crystalline mass thus obtained gave the following result:—

0·1209 gram of substance gave 0·3148 gram CO_2 and 0·0615 gram H_2O.

0·1381 gram of substance gave 6·6 c.c. N; $t = 18°$; bar. $= 747$ mm.

	Theory for $C_{14}H_{10}{\cdot}CH_3NO_3$.	Found.
C........	70·58 per cent.	71·00 per cent.
H........	5·09 ,,	5·64 ,,
N........	5·49 ,,	5·42 ,,

This substance melts with decomposition at 183°, and is identical with the anthracene methyl nitrate previously obtained by the action of nitric acid on anthracene in the presence of methyl alcohol (Trans., 1891, **59**, 648).

As the yield of the substance obtained in this way was large, its formation cannot be accounted for by the accidental presence of any traces of methyl alcohol in the acetone employed. In order that anthracene methyl nitrate may be formed in this reaction, it is necessary to suppose that the acetone is decomposed by the nitric acid into methyl nitrate and acetic acid, thus:—

$$CH_3{\cdot}CO{\cdot}CH_3 + HNO_3 + O = CH_3{\cdot}NO_3 + CH_3{\cdot}COOH.$$

The former then in the moment of its formation combines with the anthracene, forming anthracene methyl nitrate.

We propose to experiment on the action of nitric acid on other ketones in the presence of anthracene, with the view to determine whether the above interesting reaction is a general one.

Action of Nitric Acid on Anthracene in the presence of Ether.

The ether employed in this experiment was ordinary methylated ether, which had been carefully freed from alcohol by repeated treatment with sodium.

On adding anthracene to a mixture of ether, nitrobenzene, and nitric acid, a substance soon separated which, after collecting on a plug of glass wool and recrystallisation from alcohol, was obtained in thin leaflets melting at 152°, and having all the properties of anthracene ethyl nitrate (Trans., 1891, **59**, 642).

An analysis gave the following result:—

0·1376 gram gave 6·9 c.c. N; $t = 25°$; bar. = 746 mm.

	Theory for $C_{14}H_{10}{\cdot}C_2H_5NO_3$.	Found.
N........	5·20 per cent.	5·49 per cent.

The acid mother liquors from this substance, on standing, deposited a small quantity of crystalline matter melting at 183°, and found to be anthracene methyl nitrate.

0·1472 gram gave 7·2 c.c. N; $t = 20°$; bar. = 743 mm.

	Theory $C_{14}H_{10}{\cdot}CH_3NO_3$.	Found.
N........	5·49 per cent.	5·46 per cent.

The presence of the latter substance is accounted for by the fact that the ether employed contained small quantities of methyl ether or methyl ethyl ether. As anthracene methyl nitrate is far more insoluble in alcohol and other solvents than anthracene ethyl nitrate, the experiment is interesting, as indicating that, under these conditions, anthracene methyl nitrate is formed less readily than the ethyl derivative.

We hope to continue these experiments in various directions, and also propose to study the action of fuming nitric acid on ketones, as this subject has evidently not been sufficiently investigated.

LXXV.—*The Behaviour of Ethylene on Explosion with less than its own volume of Oxygen.*

By B. Lean, B.A., B.Sc. (Dalton Chemical Scholar of Owens College), and W. A. Bone, B.Sc. (Fellow of Victoria University).

Introduction.

This research, which was made at the suggestion of Professor H. B. Dixon, arose out of an observation made in the course of experiments to determine the rate of explosion of hydrocarbons when fired with an amount of oxygen insufficient to completely burn them. When ethylene was mixed with approximately its own volume of oxygen, and the mixture fired in a long lead coil, it was found that the volume of the mixtures was almost exactly doubled, the pressure in the tube having increased from 756 mm. to 1503 mm. of mercury. This result indicated that, in the main, the carbon of the hydrocarbon had been oxidised to carbonic oxide, whilst the hydrogen had been liberated as such; in fact, the result of the interaction could be represented by the equation

$$C_2H_4 + O_2 = 2CO + 2H_2.$$

This result corresponds with that arrived at originally by Dalton (*vide* Historical Résumé).

An analysis of the products showed, however, that in addition to small quantities of carbon dioxide and of some unsaturated hydrocarbon, there was also present a small percentage of some hydrocarbon which could not be absorbed by fuming sulphuric acid. We believed this hydrocarbon to be methane, formed by a partial breaking down of the ethylene molecule, as represented by one or both of the following equations:—

$$2C_2H_4 + O_2 = 2CH_4 + 2CO,$$
$$C_2H_4 = C + CH_4.$$

Another mixture of 2 vols. of ethylene with 3 vols. of oxygen was made, and, on firing this mixture in the coil, the pressure increased from 763 mm. to 1228 mm. of mercury. On analysing the products, no trace either of saturated or of unsaturated hydrocarbons could be detected. It appeared, therefore, interesting to study further the explosion of ethylene with less than its own volume of oxygen. The present paper contains the results of our investigations.

Historical Résumé.

Dalton appears to have been the first to study the incomplete combustion of ethylene. His work, the results of which are given in Part II of his New System, seems to have been overlooked by many subsequent investigators. He found that, on exploding equal volumes of ethylene and oxygen, a great increase in volume occurs, 200 vols. of the mixture, on explosion, yielding 360 vols. Furthermore, the products, when mixed with excess of oxygen and sparked, exploded, yielding carbon dioxide and water. He therefore concluded that the products of the explosion of 100 vols. of ethylene with 100 vols. of oxygen consisted mainly of carbonic oxide and hydrogen, and he estimated that about 170 vols. of each of these gases were thus formed.

Despite Dalton's work, the view became prevalent that, when hydrocarbons undergo incomplete combustion, the hydrogen is burnt to water before the carbon is oxidised.

In 1861, Kersten (*J. pr. Chem.*, **84**, 310), who seems to have been ignorant of Dalton's work, arrived at very much the same conclusions. He exploded ethylene with (1) electrolytic gas, (2) defect of air, and his results led him to conclude that the carbon is oxidised to carbonic oxide before the hydrogen is burnt.

In 1874, E. v. Meyer identified minute quantities of acraldehyde among the products of the explosion of ethylene with less than its own volume of oxygen. He explained its formation by the equation

$$C_2H_4 + CO = C_3H_4O.$$

The amount produced was too small to admit of a quantitative determination. He, however, failed to produce acraldehyde by sparking a mixture of ethylene and carbonic oxide.

The question of the incomplete combustion of hydrocarbons is, of course, connected with that of the luminosity of hydrocarbon flames. This subject has of late attracted a good deal of attention, owing principally to the researches of Teclu (*J. pr. Chem.*, **44**, 246), and of Smithells and Ingle (Trans., 1892, **61**, 204). They find that in an ethylene-air flame the interconal gases contain acetylene.

V. B. Lewes (Trans., 1892, **61**, 322) concludes that in the inner zone of a non-luminous coal-gas flame the hydrocarbons are heated up by the combustion of the hydrogen and some of the methane, and are resolved into acetylene, which, at a higher temperature, breaks up into carbon and hydrogen.

A correspondence has recently passed between Sir G. G. Stokes and H. E. Armstrong (Proc., 1892, 22) on the interactions occurring in flames. Stokes considers that at high temperatures oxygen combines with carbon in preference to hydrogen. He thinks it necessary to distinguish between the purely chemical and the thermochemical changes which occur in partial combustion. Thus in the ordinary candle flame, purely chemical changes may occur in the blue region at the base and outer portion, where the oxygen is plentiful, and the heat so liberated becomes the cause of thermochemical changes which go on in the inner portion of the flame.

Stokes writes:—"I imagine that the hydrocarbon spectrum is due to a gas formed by a pure chemical as distinguished from a thermochemical change. But what gas is it? It is commonly supposed to be acetylene. To me it seems more probable that it is marsh gas, formed by a pure chemical, not a thermochemical, change. According to my notion, this unknown gas (x, say) is a hydrocarbon, which when burnt without admixture of other hydrocarbons would show but feebly, if at all, the hydrocarbon spectrum. More especially might this be expected to take place if it were burnt at a reduced pressure, or considerably diluted with, say, nitrogen. For, in order that it should show its spectrum, its molecule must be in a state of violent agitation, which it might be expected to be if it had been born as a result of partial combustion, but would not be merely because it was going to be slain by union with oxygen." In a subsequent letter, Stokes writes—"The results of Professor Smithells seem to me to make it probable that x may be carbonic oxide."

H. E. Armstrong considers it "unwise at present to infer that the oxidation of the hydrocarbons, or the separation of carbon and also of hydrogen from them, takes place entirely in any one way."

We may here point out that Dalton, Kersten, and others have only shown that carbonic oxide and hydrogen are *eventually* obtained when ethylene is fired with its own volume of oxygen. Their results do not prove that carbonic oxide and hydrogen are the immediate products of the interaction of ethylene and oxygen.

We began this research at the Owens College, Manchester, in October, 1891. Our plan was to make various mixtures of ethylene with less than its own volume of oxygen, and after exploding them, to carefully analyse the products.

Preparation of the Gases.

Ethylene.—This was made by Erlenmeyer's method. Into a bolthead flask was introduced a mixture of 25 grams of alcohol and

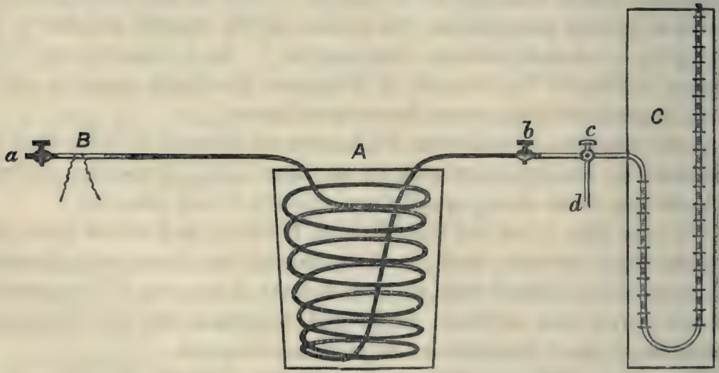
150 grams of concentrated sulphuric acid. The mixture was heated up to 160—170°, and this temperature was maintained throughout the preparation. A mixture of 1 part of alcohol and 2 parts of sulphuric acid (by weight) was slowly and continuously dropped into the generating flask from a tap funnel. The ethylene was purified by passing through two wash-bottles containing concentrated sulphuric acid, a tower containing lumps of solid moistened sodic hydrate, then through two wash-bottles containing concentrated soda solution, and lastly a second tower containing solid sodic hydrate.

Oxygen.—By heating potassic chlorate in an iron retort. The gas was purified by passing through a series of wash-bottles and towers containing sodic hydrate, either solid or in solution, and finally, to ensure the entire removal of all chlorine, a wash-bottle containing a starch and potassium iodide solution was added to serve as an indicator.

The mixtures were made and stored in a gas-holder over mercury. They were then sampled for analysis in tubes over mercury. The products of explosion were also sampled in similar manner.

Explosion of the Mixtures.

This, on account of the violence of the explosion, was effected in a leaden coil to which a mercury pressure gauge was attached. The following is a diagram of the apparatus The coil A (capacity = 2·1 litres) was contained in a bucket of water. The coil had a glass firing piece B, and carried steel taps *a*, *b*. *c* is a glass tail tap connecting the coil with the manometer C.



The gases were introduced into the coil through the steel tap *a*, the products were drawn off for analysis through *d*.

The coil was well dried before use, and tested to prove that all joints were tight.

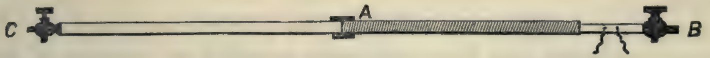
Seven different mixtures of ethylene and oxygen were made.

A. We made a mixture of 100 vols. of ethylene with 50 vols. of oxygen. The coil was filled with this mixture, and sparked. The gases only seemed to burn in the neighbourhood of the wires, and on connecting with the manometer no change in pressure was recorded. We then introduced a little electrolytic gas at the firing piece end, in order, if possible, to start an explosion. On sparking, the flame started at the firing piece, but on connecting with the manometer, a slight decrease in pressure was recorded, showing that only the electrolytic gas in the firing piece had been fired. We concluded that a mixture of ethylene with half its volume of oxygen does not explode.

B. We next made a mixture of 100 vols. of ethylene with 65 vols. of oxygen.

Experiment 1.—Introduced the mixture into the coil, and sparked. A flame seemed to start at the firing piece, but on connecting with the manometer, only a very slight increase in pressure (20 mm.) was recorded, showing that the mixture had merely burned in the neighbourhood of the wires. We then sent a little electrolytic gas in at the firing piece end, and sparked. The mixture did not explode.

Experiment 2.—We substituted a wider tube for the coil. AB is metal tube carrying a glass firing piece, and a steel tap B. This is joined to a wide glass tube, AC, by means of a metal joint at A, and on to this is fixed a steel tap, C.



The mixture was introduced into the apparatus, and sparked. The flash, which travelled rapidly along AC, was of intense brightness and was succeeded by a dense black cloud of liberated carbon. The products were displaced by a current of air, and burnt with a fairly luminous flame at C.

This mixture, therefore, seemed to be near the limit of detonation, it being possible to fire it in the wide tube, but not in the narrower coil.

C. We next made a mixture of 100 vols. of ethylene with 70 vols. of oxygen.

Experiment 1.—Filled the coil with the mixture and sparked. The mixture burnt in the neighbourhood of the wires only. We then introduced a little electrolytic gas at the firing piece end, and again sparked. The mixture was fired, and the manomoter showed an increase in pressure of 480 mm. Carbon was deposited on the glass of the firing piece.

Experiment 2.—We tried to fire the original mixture, after filling the coil at the ordinary temperature, and then heating the water surround ing it up to 85°. On so doing, the gases in the coil were found to be under a pressure of 184 mm. above that of the atmosphere. The mixture was then sparked, but was not fired. On introducing electrolytic gas, however, and sparking, the mixture was fired as in the previous experiment, and the manometer registered an increase in pressure of 466 mm.

D. Made a mixture of 100 vols. of ethylene with 75 vols. of oxygen.

Experiment.—The coil was filled with the mixture and sparked. No explosion. Introduced a little electrolytic gas at the firing piece end, and sparked. The mixture was fired, and the manometer recorded an increase in pressure of 546 mm. Carbon was deposited in the firing piece.

E. Made a mixture of 100 vols. of ethylene with 90 vols. of oxygen.

Experiment.—The coil was filled with the mixture; on sparking, the flame seemed to start in the firing piece, but did not travel far, as the manometer only recorded an increase in pressure of about 20 mm. On introducing a little electrolytic gas and sparking, the mixture exploded, and the manometer recorded an increase in pressure of 512 mm. of mercury. Much less carbon was deposited than in the previous experiments.

F. Made a mixture of 100 vols. of ethylene with 95 vols. of oxygen.

Experiments.—Filled the coil with the mixture, and sparked. The mixture exploded, and the manometer recorded an increase in pressure of 703 mm. of mercury, the barometer standing at 776·8 mm. On repeating the experiments, the increase in pressure recorded was 690 mm. There was scarcely any carbon deposited.

G. This is the mixture which was employed at the outset of the research (see Introduction); it was intended to contain equal volumes of oxygen and ethylene; analysis, however, showed that there was rather less oxygen than ethylene, the real composition being 100 vols. of ethylene to 96·5 vols. of oxygen. The increase in pressure on explosion was 747 mm. of mercury, the barometer standing at 756 mm.

Analysis of the Gases.

Apparatus.—The apparatus employed was a modified form of the McLeod apparatus (described in *Phil. Trans.*, 1884, Part II). This consists essentially of a eudiometer, connected at its base with a barometer; both eudiometer and barometer are water-jacketed, so that the temperature may be kept constant throughout the analysis. Both eudiometer and barometer are connected with a mercury reservoir, which may be raised or lowered as occasion may require. The upper end of the eudiometer is connected by means of a glass capillary tube with a laboratory vessel, into which the gases are sent for purposes of absorption.

The eudiometer and laboratory vessel are closed by glass taps. Steps were taken to apply a correction for the gas left in the capillary tube between the two taps after each absorption. The taps were lubricated with glacial phosphoric acid.

Before each analysis, the eudiometer was washed out, first with dilute sulphuric acid and then with water.

Readings were made by artificial light.

Action of Absorbing Liquids on Gases.

The importance of this question became apparent to us while analysing the mixture F, the first we analysed. We found that fuming sulphuric acid undoubtedly absorbs oxygen, as will be shown below.

Action of Fuming Sulphuric Acid on Oxygen.—We analysed the mixture F in two ways: (1) by first absorbing the ethylene with fuming acid, and afterwards the oxygen with alkaline pyrogallol; (2) by first absorbing the oxygen, and then the ethylene. Two determinations were made by each method. The results were :—

	I. Removal of ethylene first.		II. Removal of oxygen first.	
	(1.)	(2.)	(1.)	(2.)
Ethylene	51·65	51·75	48·73	48·55
Oxygen	43·21	42·94	45·57	46·22

The question at once arose, whether fuming sulphuric acid has any action on oxygen. This question was decided by further experiment :—

We took a sample of oxygen prepared from potassic chlorate, and, after washing with dilute potash solution to remove traces of chlorine, we treated it in the laboratory vessel with fuming sulphuric acid, and then with dilute potash again. We found that a considerable absorption had occurred; this could not be due to the drying of the gases, as the eudiometer was kept saturated with moisture:—

Oxygen taken after first treatment with dilute potash	=	240·5 volumes.
Absorption by fuming acid	=	2·7 ,,

The oxygen was further subjected to the action of fuming acid, and a further absorption of 1·9 volumes occurrred. The gas was in contact with the fuming acid about 15 minutes in each case.

We tested the action of fuming acid, in a similar manner, on hydrogen and nitrogen, but found no absorption.

Action of Alkaline Pyrogallol on Ethylene.—A sample of ethylene was introduced into the laboratory vessel, and allowed to stand over alkaline pyrogallol for a few minutes, in order to remove any traces of oxygen which might be present. The gas was then measured. It was treated in the laboratory vessel with fresh alkaline pyrogallol and re-measured at successive intervals of 20 minutes. On 170 vols. of gas taken we found no absorption.

We also found that alkaline pyrogallol has no action on nitrogen.

Action of Strong Potash Solution on Ethylene.—We examined this at the suggestion of Professor Dixon. We introduced a volume of ethylene into the laboratory vessel and then treated it with dilute potash, in order to remove any traces of carbon dioxide or sulphur dioxide which might be present, then measured the gas, and subjected it in the laboratory vessel to the action of saturated potash solution. We found that no absorption occurred, although in one experiment we allowed the gas to remain over the concentrated potash solution for 16½ hours.

Analysis of the Original Mixtures.

In each case we adopted one or both of the following methods:—

I. *Absorption Method.*—This consisted in: (1) the removal of oxygen by means of alkaline pyrogallol; (2) the removal of ethylene by fuming sulphuric acid. Nitrogen by difference.

II. *Explosion Method.*—This consisted in adding excess of air free from carbon dioxide and exploding, determining: (1) the contraction on explosion, that is, C; (2) the absorption by potash after explosion, that is, A. In this method it is necessary to add a very large excess of air (nearly 20 times the volume of ethylene present, if the gases are exploded under normal pressure) in order to prevent the formation of nitric acid on explosion. If this be done, C should = A.

Mixture C. Explosion Method.—The following are the results of six determinations for ethylene by this method:—

	(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	Mean.
Ethylene..	55·64	56·66	56·12	56·16	56·29	56·30	56·03 p. c.

Nitrogen.—This was determined, by exploding the gas with excess of air, removing afterwards both the carbon dioxide and the oxygen at one and the same time by alkaline pyrogallol. The result was N = 4·53 per cent. This agrees well with determinations of nitrogen made by the absorption method, where N = 4·76; 4·33; 4·43 per cent.

Hence, N (mean of the four determinations) = 4·51 per cent.

Oxygen.—By difference = 39·46. This agrees well with the results obtained by both explosion and absorption methods; the mean of five determinations being 39·22 per cent.

Results.	Ethylene..........	56·03
	Oxygen...........	39·46
	Nitrogen..........	4·51

Mixture D.—In the case of this mixture, air was accidentally introduced into one of the two sample tubes collected; consequently we were left with only one tube to analyse. We however, obtained one very good analysis by the explosion method:—

Gas taken	73·65			
Air added	611·40		Ethylene....	54·18
C............	79·70	This gives	Oxygen.....	41·52
A	79·92		Nitrogen....	4·30
Nitrogen left..	486·89			

The result for ethylene was confirmed by two other analyses by the explosion method. Here, C_2H_4 = 54·08; 54·55. These analyses were, however, not completed, and we decided to take the results of the one complete analysis.

Mixture E.—Five analyses were made, two by the absorption and three by the explosion method; one of the latter was, however, not completed, and only gave results for ethylene.

Results.

	Absorption method.		Explosion method.			Mean.
	(1.)	(2.)	(1.)	(2.)	(3.)	
Ethylene....	49·30	49·17	50·58	49·66	50·12	49·77
Oxygen.....	45·51	45·14	45·72	46·86	—	45·81
Nitrogen....	5·19	5·69	3·70	3·48	—	4 42

Mixture F.—Two analyses by absorption method. Results:—

	(1.)	(2.)	Mean.
Ethylene	48·73	48·55	48·64
Oxygen...........	45·57	46·22	45·84
Nitrogen.........	5·70	5·33	5·52

Mixture G.—One analysis by explosion method. Results:—

Ethylene..............	49·41
Oxygen..............	47·69
Nitrogen.............	2·90

Disregarding the nitrogen, we find by calculation:

Mixture	C	contains	100	vols. C_2H_4	to	70·44	vols O_2.
,,	D	,,	100	,,	,,	76·63	,,
,,	E	,,	100	,,	,,	92·04	,,
,,	F	,,	100	,,	,,	94·26	,,
,,	G	,,	100	,,	,,	96·52	,,

Analysis of the Products.

The analysis of the products constituted the most important part of our work.

Method.—The method employed was (1) removal of carbon dioxide by potash; (2) removal of unsaturated hydrocarbons, &c., with fuming sulphuric acid; (3) addition of measured amounts of oxygen and air; (4) explosion; (5) determination of the contraction (C) and the absorption (A).

The nitrogen, except in the case of products G, was specially determined by adding excess of air to a measured amount of the gas, and exploding, afterwards removing the carbon dioxide produced and the excess of oxygen by alkaline pyrogallol. The residual nitrogen was then measured. Knowing the amount of nitrogen in the air added, the amount of nitrogen present originally in the mixture could thus be determined.

Calculation from Results.—Below will be given the results of the analyses in percentages, for carbon dioxide, unsaturated hydrocarbons, C and A. The results obtained for C and A cannot, as will be shown below, be explained if, after removal of the carbon dioxide and unsaturated hydrocarbons, only carbonic oxide and hydrogen remain in the mixture. There must be some saturated hydrocarbon present. It is most reasonable to assume this to be methane. We shall, later on, have something further to say about the composition of the unsaturated hydrocarbons.

Products of G.—The analysis of these products had to be modified somewhat, owing to the fact that the amount of carbon dioxide present was very small, and no unsaturated hydrocarbon was present.

Carbon Dioxide.—The amount present being so small, it was specially determined in large volumes of the gases. Results:—

	(1.)	(2.)	(3.)	(4.)	Mean.
CO_2	0·35	0·27	0·33	0·34	0·33 per cent.

Unsaturated Hydrocarbons.—None present. No alteration in volume after treating 367·7 vols. of the product with fuming acid (after removal of the carbon dioxide). This result was confirmed by other determinations.

Residual Gases.—Fresh amounts of the mixed gases were taken and exploded with excess of air free from carbon dioxide, and C and A determined. Excess of oxygen was removed by alkaline pyrogallol, and the residual nitrogen measured.

Results—

	(1.)	(2.)	Mean.
C	99·62	99·88	99·75
A	50·22	50·68	50·45
Nitrogen.....	0·85	0·70	0·77

We therefore have 0·33 + 0·77 = 1·10 per cent. of carbon dioxide and nitrogen; hence the residual gases = 98·90 per cent.

From the absorption, 50·45 per cent., must be subtracted 0·33 per cent. due to carbon dioxide present in the gases before explosion; hence A = 50·12 per cent.

From the above data, if we calculate on the assumption that only carbonic oxide and hydrogen are present, we find—

$$\left.\begin{array}{ll}\text{Carbonic oxide} \;.. & 50{\cdot}12 \\ \text{Hydrogen} \;....... & 49{\cdot}79\end{array}\right\} \quad \text{Total} \;...... \quad 99{\cdot}91$$

This is 1·01 in excess of the total volume (98·90); hence there is some other body, presumably methane, present.

Calculating on this last assumption, we have—

Carbonic oxide	49·11	per cent.
Hydrogen	48·78	,,
Methane	1·01	,,

Products of F.—In all, four analyses were made, two of which were not completed, but gave results for carbon dioxide and unsaturated hydrocarbons.

Results.

	(1.)	(2.)	(3.)	(4.)	Mean.
Unsaturated hydrocarbons.	2·31	1·92	2·23	2·10	2·14
Carbon dioxide...........	—	1·09	0·75	0·99	0·94
C......................	96·85	95·93	—	—	96·39
A......................	48·76	49·40	—	—	49·08

Nitrogen. Two Determinations.

	(1.)	(2.)
Volume of gas taken...	60·4	56·9
,, air added ..	319·15	335·7
Residual nitrogen	254·02	266·9
Per cent. nitrogen.....	2·59	2·39

Mean for nitrogen = 2·49 per cent.

Calculating from the above data, we have—

Unsaturated hydrocarbons ..	2·14
Carbon dioxide	0·94
Methane	2·55
Carbonic oxide	46·53
Hydrogen	45·35
Nitrogen.................	2·49

Products of E.—Two full analyses were made, which afforded very concordant results. In another analysis, the carbon dioxide and unsaturated hydrocarbons alone were determined.

Results.

	(1.)	(2.)	(3.)	Mean.
Unsaturated hydrocarbons	2·68	2·82	2·84	2·78
Carbon dioxide	1·28	1·35	1·10	1·24
C..........................	93·84	93·98	—	93·91
A..........................	50·30	50·33	—	50·31

Nitrogen.—Four determinations were made, with the following results:—

	(1.)	(2.)	(3.)	(4).
Volume of gas taken..	47·7	44·2	57·6	81·6
,, air added .	257·35	258·3	293·4	365·55
Residual nitrogen	204·75	205·15	233·69	290·96
Per cent. nitrogen....	2·5	1·90	2·80	2·22

Mean for nitrogen = 2·35 per cent.

Calculating from the above data, we have—

Unsaturated hydrocarbons ..	2·78
Carbon dioxide	1·24
Methane.......	2·52
Carbonic oxide....	47·79
Hydrogen	43·32
Nitrogen.................	2·35

Products of D.—Three full analyses were made. In a fourth analysis everything, except A, was determined, whilst in another analysis the amounts of carbon dioxide and unsaturated hydrocarbons alone were determined.

Results.

	(1.)	(2.)	(3.)	(4.)	(5.)	Mean.
Unsaturated hydrocarbons	4·63	4·30	3·92	2·42	3·58	3·77
Carbon dioxide	2·19	3·18	2·82	2·98	2·84	2·80
C	93·02	91·86	92·51	92·78	—	92·54
A	49·03	48·95	47·82	—	—	48·61

Nitrogen. Two Determinations. Results.

	(1.)	(2.)
Volume of gas taken.	45·0	48·1
,, air added.	286·75	281·1
Residual nitrogen ...	228·28	224·78
Per cent. nitrogen ...	3·24	2·97

Mean for nitrogen = 3·10 per cent.

Calculating from the foregoing data, we have—

Unsaturated hydrocarbons ..	3·77
Methane	3·77
Carbon dioxide	2·80
Carbonic oxide	44·84
Hydrogen	41·72
Nitrogen..................	3·10

Products of C.—Two full analyses were made.

Results.

	(1.)	(2.)	Mean.
Unsaturated hydrocarbons .	5·58	5·49	5·53
Carbon dioxide	1·52	1·74	1·63
Nitrogen	5·35	4·97	5·16
C	95·68	95·28	95·48
A	44·33	44·43	44·38

Calculating from these data, we have—

Unsaturated hydrocarbons...	5·53
Methane	5·96
Carbon dioxide	1·63
Carbonic oxide	38·85
Hydrogen	43·30
Nitrogen.................	5·16

We may now tabulate the results of our analyses.

Composition of the Mixtures fired.

Mixture.	C.	D.	E.	F.	G.
Ethylene	56·03	54·18	49·77	48·64	49·41
Oxygen	39·46	41·52	45·81	45·84	47·69
Nitrogen	4·51	4·30	4·42	5·52	2·90

Composition of the Products of Explosion.

Mixture.	C.	D.	E.	F.	G.
Unsaturated hydrocarbons	5·53	3·77	2·78	2·14	—
Methane	5·96	3·77	2·52	2·55	1·01
Carbon dioxide	1·63	2·80	1·24	0·94	0·33
Carbonic oxide	38·85	44·84	47·79	46·53	49·11
Hydrogen	43·30	41·72	43·32	45·35	48·78
Nitrogen	5·16	3·10	2·35	2·49	1·01

Liberation of Carbon.—The blackening of the glass firing piece, when the mixtures C, D, and E were fired appeared to prove the liberation of carbon. To confirm this conclusion, a mixture of 100 vols. of ethylene and 90 vols. of oxygen was exploded in the coil, and the products of the explosion were immediately expelled by a current of air, and driven through a tube packed with cotton wool. The wool was rendered completely black by the very finely divided carbon which it abstracted from the gases.

Unsaturated Hydrocarbons.—In the former part of our paper, we stated that Smithells and Ingle, and independently V. B. Lewes, had arrived at the conclusion that acetylene is formed in the inner zone of the non-luminous flame, owing to the breaking up of the hydrocarbons. We therefore were led to see whether we could detect acetylene among the products of the explosion of ethylene with less than its own volume of oxygen.

The ordinary method for the detection of acetylene (by means of an ammoniacal solution of cuprous chloride) cannot here be employed, on account of the presence of carbonic oxide among the products. We therefore employed a solution of silver chloride in ammonia. On passing carbonic oxide through this solution for a considerable time, we found that it became brown and just a trace of a dark precipitate was formed. Acetylene, on the other hand, at once acted on the solution, forming a yellowish-white precipitate of silver acetylide. We found that we could easily, in this way, detect 0·25 per cent. of acetylene in an experimental mixture containing a large volume of carbonic oxide.

Experiment.—We made a mixture of 100 vols. of ethylene and 90 vols. of oxygen, and exploded the same in the coil. After explosion, we passed the products through an ammoniacal solution of silver chloride; silver acetylide was at once formed. We confirmed this by decomposing a portion of this precipitate with concentrated hydrochloric acid, when the characteristic smell of acetylene was obtained. Another portion was dried, and then heated, when it detonated. There could, therefore, be no doubt that acetylene is formed when ethylene is exploded with less than its own volume of oxygen.

In view of the possible connection between the liberation of carbon and the formation of acetylene, it appeared of interest to test the presence of carbon and acetylene in the products of the explosion of methane with less than its own volume of oxygen. Methane will not detonate unless it is fired with very nearly its own volume of oxygen. Bearing in mind the fact that the carbon of a hydrocarbon appears to be oxidised before the hydrogen, we did not expect to find any carbon liberated when this mixture was fired, and doubted whether any acetylene would be found among the products of the explosion. Such was the case; neither carbon nor acetylene could be detected.

In view of our results, we are inclined to suggest that the acetylene, formed in the combustion of ethylene with less than its own volume of oxygen, originates in the union of nascent hydrogen with nascent carbon at the very high temperature of the explosion. Such a formation of acetylene appears more probable than that it is produced by the direct decomposition of ethylene molecules.

General Conclusions.

1. Our results indicate that when ethylene is fired with its own volume of oxygen, carbonic oxide and hydrogen are eventually obtained, the result of the interaction being represented by the equation

$$C_2H_4 + O_2 = 2CO + 2H_2 \quad \ldots\ldots\ldots\ldots \quad (a).$$

This is in accordance with the previous work of Dalton, Kersten, and E. v. Meyer.

2. When ethylene is fired with less than its own volume of oxygen, we find that methane is formed. The quantity thus produced increases as the quantity of oxygen in the original mixture decreases. This formation of methane has a bearing upon the subject of the interaction occurring in flames, and is interesting in connection with the

expression of opinion on the part of Sir G. G. Stokes, cited in the earlier portion of this communication.

We suggest that the heat liberated by the main reaction produces a decomposition of some of the unburnt ethylene into methane and carbon, analogous to the decomposition which ethylene undergoes when passed through a red hot tube.

The simplest formation is that represented by the equation

$$C_2H_4 = CH_4 + C \ldots\ldots\ldots\ldots\ldots\ldots \quad (b).$$

Methane might also be produceed by partial oxidation, according to the equation

$$2C_2H_4 + O_2 = 2CH_4 + 2CO \ldots\ldots\ldots\ldots \quad (c).$$

3. Carbon is liberated.

4. Unsaturated hydrocarbons are formed, of which acetylene forms an important part. We suggest that the formation of acetylene is due to a secondary reaction between the nascent hydrogen formed according to equation (*a*) and the nascent carbon liberated according to equation (*b*), thus

$$2C + 2H = C_2H_2.$$

In conclusion, we have great pleasure in thanking Professor Dixon for many fruitful suggestions, and for the facilities he has afforded us in the prosecution of our research.

Owens College, Manchester.

LXXVI.—*On the Lowering of the Freezing Points of Cadmium, Bismuth, and Lead when alloyed with other Metals.*

By C. T. Heycock, M.A., and F. H. Neville, M.A.

In the Proceedings of the Chemical Society, No. 88, Session 1890–91, we published a short account of the results of the application of Raoult's method to alloys in which bismuth, cadmium, and lead were the solvent metals.

We have since then revised and repeated many of the experiments on which that summary was based, and propose in this paper to give the experimental numbers themselves. The method of experiment has been fully described in previous papers (Trans., 1890, **57**, p. 376). We need only add the fact that in all cases of difficult solubility, or when oxidation of the added metal was to be feared, the alloys were made by placing weighed quantities of the two metals in a hard glass tube, exhausting and sealing the tube. The tube and its contents were then heated to a red heat and well shaken. The alloys made in this way were afterwards added to the bulk of the solvent in the block.

As the freezing points of cadmium and lead are nearly 100° higher than that of tin, our thermometrical difficulties were greater, and there is no doubt that further experiment would improve some of the numbers obtained. The zeros of the thermometers, as in our previous experiments, were fixed by heating for 18 days either in boiling mercury or sulphur.

In the following tables we have retained the column headed "Atomic Fall." By this term, we express the ratio of the fall in freezing point of the alloy below that of the pure solvent, to the number of foreign atoms present per 100 of solvent.

Expressed as a formula:—if t and t' be the freezing points (in degrees centigrade) of the pure solvent and of the alloy respectively and n be the number of atoms of foreign metal present per 100 atoms of solvent, then the *atomic fall* is $= \frac{t - t'}{n}$. This number gives the average effect produced by an atomic weight of the dissolved body at different concentrations.*

From a consideration of the following tables and of the experiments in which tin was the solvent (Trans., 1890, **57**, 376), it will be seen that the atomic fall is independent of the concentration, when the solution is dilute. As the concentration increases, a gradual change, however, takes place in the value of the atomic fall.

In a few cases, such as that of gold in cadmium or tin, and of mercury in cadmium, there is an increase in the atomic fall as the concentration increases, but in most cases the reverse is true.

Of the various causes of change in the atomic fall with increasing concentration the following appear to be most worthy of consideration:—

(*a.*) Van't Hoff's theory in its simplest form assumes that the dissolved body is in the condition of a perfect gas; but bearing in mind the enormous osmotic pressures at work, it seems almost certain that as the concentration increases, deviations from the gaseous laws analogous to those investigated by Amagat would show themselves. For moderate concentrations we might expect that this cause would decrease the osmotic pressure and consequently the atomic fall.

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* In the tables, the atomic fall is often given for very dilute solutions, but it is evident that in these cases the experimental errors are magnified by the process of calculation.

(*b.*) Van't Hoff's theory also assumes that, however the concentration increases, the space available for the diffusion of the dissolved substance regarded as a gas, remains what it was at first, namely the original volume of the solvent, so that the osmotic pressure is, by Boyle's law, directly proportional to the amount of dissolved body added: but this is an assumption which seems improbable. A careful determination of the densities of the liquid alloys at their melting points would throw some light on this point, but we have not at present been able to make experiments in this direction.

(*c.*) It might be expected that increasing concentration would cause polymerisation in the molecules of the dissolved body somewhat analogous to that shown by the vapours of acetic acid, iodine, and hydrogen fluoride. Hitherto we have found but little evidence of this sort of action, the atomicity of the dissolved molecule in concentrated and dilute solutions appearing to be the same.

(*d.*) Atomic falls smaller than theory demands may also be due to that portion of the solvent which solidifies at the moment of freezing, carrying with it some of the dissolved metal. This would decrease the osmotic pressure, and, therefore, the amount of work to be done before freezing can occur; the fall in the freezing point would, therefore, be less.* The above action is analogous to the well known fact that many precipitates carry soluble substances down with them.

We do not at present see a satisfactory method of estimating the amount of foreign metal carried down with the solvent in these cases, on account of the difficulty of separating the solid from the mother liquor. An extreme case of this action is to be found when lead is alloyed with thallium; the two metals mix readily, and as they cool there is no perceptible separation. The freezing point of such an alloy is identical with that of pure lead.

The same cause may in extreme cases produce a rise instead of a fall in the freezing point, as we have observed with antimony in tin, antimony in bismuth, and silver in cadmium. For so long as the precipitate which separates out is poorer in foreign metal than the liquid, there will be some fall, but if on the other hand a precipitate, rich in the foreign metal, separates out of a dilute solution, the sign of the work which has to be done is reversed and a rise may be expected. In such cases the precipitate is probably a chemical compound of the two metals. (See Table XIX, p. 900.)

(*e.*) The remaining cause that we venture to suggest as a possible one would alone, if correct, account in many cases for the observed decrease in the atomic fall with increasing concentrations. It is due to the fact that Van't Hoff's formula $\delta\theta = \kappa n \theta^2$, where $\delta\theta$ is fall in freezing point, κ a constant, n proportional to the quantity of dissolved metal, and θ the absolute freezing point of the pure solvent, is strictly true only when the solution is infinitely dilute. For finite concentrations, similar reasoning to that by which the above formula was obtained seems to lead to the formula $\delta\theta = \kappa n\theta(\theta - \delta\theta)$. Making this correction, and using n to express the number of atoms of foreign metal per hundred of solvent, we get the following values for the atomic fall:—

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* Van't Hoff (*Zeit. physikal. Chem.*, **5**, 334) and A. van Bijlert (*ibid.*, **8**, 343) give the same explanation, and support it by experimental evidence.

TABLE I.

Values of n.	Theoretical atomic falls.			
	Tin.	Bismuth.	Cadmium.	Lead.
0............	3·0	2·08	4·5	6·5
1............	2·98	2·07	4·47	6·43
5............	2·91	2·04	4·34	6·17
10............	2·83	2·00	4·18	5·87
20............	2·68	1·93	3·91	5·35

These values are all calculated on the assumption that the molecule of the substance in solution contains 1 atom.

When we take a general survey of the atomic falls given by the tables below, and compare them with the molecular falls predicted by the theory of osmotic pressure, we see not only that the experimental numbers are identical in a great many cases with the theoretical fall produced by a monatomic molecule, but that the experimental numbers, while often lower, *are never higher* than the theoretical number (see Table XLII, p. 911). This is an important point in favour of the osmotic theory of solution, for this theory, whilst readily explaining a low atomic fall by the hypothesis of the dissolved molecule containing more than 1 atom, assigns a superior limit, corresponding to the state in which the molecules in solution contain each 1 atom of the dissolved body. With these numbers before us, it seems impossible to resist the conclusion that the process of solution consists essentially in the disintegration of the dissolved body, and its uniform diffusion through the solvent as a gas, in other words, that the "physical theory of solution" is correct. The characteristic assumption of the "hydrate theory of solution," that a chemical union of the dissolved body with the solvent is an essential part of the process, is of no use as an aid in predicting the numerical results. But in some cases, for instance, that of gold dissolved in cadmium, and a few others, we have no doubt that the molecule in solution contains atoms of both metals (*vide* Gold in Cadmium, this vol., p. 902).

It is noteworthy that even when the atomic fall of a metal is abnormally small, as for example, that of tin in lead, it has the same value at a very great dilution as at a moderate concentration. We think that our work on the triple alloys of gold, cadmium, and tin (Trans., 1891, **59**, 936) throws considerable light on these small atomic falls. Without attempting to discuss each in detail, it is clear that such an atomic fall as that produced by gold in cadmium (Table XXIII, p. 902) can be explained by the assumption that the molecule in solution is Au_3Cd_3, but that a certain small pressure of molecules of the type Au is, by the principle of chemical equilibrium, necessary to maintain the stability of the compound. We mention this case because we have isolated the body AuCd. But many other cases might be brought forward, such as that of mercury in cadmium, where the existence of free mercury, together with the molecule Cd_xHg_2, suffices to explain the phenomena. In other cases, it is not necessary to assume the existence of cadmium in the dissolved molecule. Perhaps the most satisfactory method of ascertaining in each case whether the solvent combines with the dissolved body is to study the behaviour of the two metals when they are dissolved together in a third (*vide* paper on Triple Alloys, *loc. cit.*). We have in this way established the existence of several alloys which are definite chemical compounds; we hope shortly to communicate the results to the Society.

BISMUTH AS SOLVENT.

TABLE II.—*Sodium in Bismuth.*

Thermometer, Müller.

Weight of bismuth in block.	Weights of sodium added in succession.	Total weight of sodium in block.	Freezing point of solution.	Atoms of sodium per 100 of bismuth.	Atomic fall.
50			266·34°		
”	0·0452	0·0452	264·86	0·825	1·79
”	0·087	0·132	261·43	2·41	2·04
”	0·0863	0·218	258·06	4·00	2·07

Magnesium in Bismuth.

Magnesium dropped into red hot bismuth dissolves with incandescence, and attacks the glass. The alloy is very difficult to separate from the tube. Alloys of magnesium and bismuth thus made do not appear to lower the freezing point of bismuth.

Aluminium in Bismuth.

When aluminium-bismuth alloys are made and added to molten bismuth in the usual way, there is a small fall in the freezing point of about 0·25° per atom, but the experiments need confirmation.

Table III.—*Copper in Bismuth.*

Thermometer, Müller.

Series I.

Weight of bismuth in block.	Weights of copper added in succession.	Total weight of copper in block.	Freezing point of solution.	Atoms of copper per 100 of bismuth.	Atomic fall.
50			266·23°		
52	0·0404	0·0404	265·87	0·259	1·35
54	0·078	0·1184	265·47	0·729	1·04
56	0·101	0·2194	265·47	saturated	

Series II.

50			266·75°		
52	0·050	0·050	266·34	0·32	1·28
54	0·0492	0·0992	266·14	0·614	0·993
59		0·0992	266·17	0·565	1 08
61	0·0560	0·1552	266·12		

Probably the first atomic fall alone in each series represents the true fall in an unsaturated solution.

Table IV.—*Zinc in Bismuth.*

Thermometer, Müller.

Weight of bismuth in block.	Weights of zinc added in succession.	Total weight of zinc in block.	Freezing point of solution.	Atoms of zinc per 100 of bismuth.	Atomic fall.
50			266·17°		
52	0·0808	0·0808	265·59	0·501	1·16
54	0·1305	0·2113	264·24	1·260	1·53
56	0·1340	0·3453	262·83	1·99	1·68
58	0·211	0·5563	260·84	3·09	1·73
60	0·345	0·901	258·21	4·84	1·64
62	0·667	1·568	254·84	8·15	1·39

TABLE V.—*Arsenic in Bismuth.*

Thermometer, Müller.

Series I.

Weight of bismuth in block.	Weights of arsenic added in succession.	Total weight of arsenic in block.	Freezing point of solution.	Atoms of arsenic per 100 of bismuth.	Atomic fall.
50			266·54°		
52	0·0484	0·0484	266·34	0·258	0·775
54	0·1322*	0·1806	265·59	0·928	1·024
58	0·3055	0·4861	265·00	2·325	0·662
62	0·2995	0·7856	265·04	3·51	

Series II.

50			266·55°		
56	0·094	0·094	266·24	0·466	0·665
62	0·086	0·180	265·93	0·805	0·770
68	0·1735	0·3535	265·52	1·442	0·714
74	0·0931	0·4464	265·33	1·670	0·730

These numbers point to the molecule As_3, as the observed fall is about one-third of the theoretical atomic fall.

TABLE VI.—*Palladium in Bismuth.*

Thermometer, Müller.

Weight of bismuth in block.	Weights of palladium added in succession.	Total weight of palladium in block.	Freezing point of solution.	Atoms of palladium per 100 of bismuth.	Atomic fall.
50			266·53°		
52	0·0504	0·0504	266·24	0·191	1·52
54	0·1015	0·1519	265·51	0·550	1·85
56	0·1055	0·2574	264·72	0·905	2·00
58	0·1840	0·4414	263·28	1·49	2·18
60	0·15	0·5914	262·49	1·94	2·08
62	0·131	0·7224	261·57	2·295	2·16

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* Probably an error in weighing.

TABLE VII.—*Silver in Bismuth.*

Thermometer, Müller.

Weight of bismuth in block.	Weights of silver added in succession.	Total weight of silver in block.	Freezing point of solution.	Atoms of silver per 100 of bismuth.	Atomic fall.
50			265·98°		
52	0·1776	0·1776	264·61	0·664	2·06
54	0·2028	0·3804	263·24	1·387	1·98
57	0·3615	0·7419	261·1	2·53	1·93

Thallium was now added to the above solution of silver, and as thallium has not been tried again in pure bismuth, we give the result here :—

	Thallium added in succession.	Total thallium.			
	0·164	0·164	260·49	0·294	2·06
	0·3385	0·5025	259·31	0·898	2·00

TABLE VIII.—*Cadmium in Bismuth.*

Thermometer, Müller.

Weight of bismuth in block.	Weights of cadmium added in succession.	Total weight of cadmium in block.	Freezing point of solution.	Atoms of cadmium per 100 of bismuth.	Atomic fall.
50			266·44°		
,,	0·029	0·029	266·24	0·1087	1·84
,,	0·0648	0·0938	265·77	0·352	1·90
,,	0·1826	0·2764	264·31	1·037	2·05
,,	0·1782	0·4546	262·95	1·705	2·05
,,	0·1800	0·6346	261·46	2·38	2·09
,,	0·499	1·134	257·59	4·252	2·08

TABLE IX.—*Tin in Bismuth.*

Thermometer, Müller.

Weight of bismuth in block.	Weights of tin added in succession.	Total weight of tin in block.	Freezing point of the solution.	Atoms of tin per 100 of solution.	Atomic fall.
50			265·83°		
”	0·0449	0·0449	265·51	0·1598	2·00
”	0·0846	0·1295	264·88	0·4604	2·06
”	0·2271	0·3566	263·16	1·268	2·11
”	0·2672	0·6258	261·09	2·225	2·13

To this mixture lead was now added.

Weight of bismuth in block.	Weights of tin added in succession.	Total weight of tin in block.	Freezing point of the solution.	Atoms of tin per 100 of solution.	Atomic fall.
	0·497 Pb	0·497	258·72	1·11	2·08
	0·365	0·862	257·16	1·754	2·12

TABLE X.—*Antimony in Bismuth.*

Thermometer, Müller.

Weight of bismuth in block.	Weights of antimony added in succession.	Total weight of antimony in block.	Freezing point of solution.	Atoms of antimony per 100 of bismuth.	Atomic *rise.*
50			266·42°		
52	0·0675	0·0675	267·06	0·2369	2·70
54	0·080	0·1475	267·88	0·477	3·06
56	0·1955	0·3430	269·63	1·072	2·99
58	0·604	0·947	275·16	2·856	3·06

See notes on Silver in Cadmium, Table XIX (p. 900).

TABLE XI.—*Platinum in Bismuth.*

Thermometer, Müller.

Weight of bismuth in block.	Weights of platinum added in succession.	Total weight of platinum in block.	Freezing point of solution.	Atoms of platinum per 100 of bismuth.	Atomic fall.
50			266·45°		
52	0·0992	0·0992	266·02	0·206	2·09
54	0·220	0·3192	265·06	0·638	2·18
56	0·298	0·6176	264·26	1·19	1·84*
61		0·6176	264·26	1·093	1·9*
66		0·6176	264·29	1·01	2·14
71		0·6176	264·42	0·939	2·16

* Saturated.

TABLE XII.—*Gold in Bismuth.*

Thermometer, Müller.

Weight of bismuth in block.	Weights of gold added in succession.	Total weight of gold in block.	Freezing point of solution.	Atoms of gold per 100 of bismuth.	Atomic fall.
50			266·42°		
52	0·181	0·181	265·62	0·371	2·16
54	0·149	0·330	265·10	0·6445	2·05
56	0·354	0·684	263·74	1·28	2·09
58	0·301	0·985	262·73	1·81	2·04

A second series carried as far as 5 atoms of gold gave a constant atomic fall of 2°.

Thallium in Bismuth. (See end of Table VII.)

Lead in Bismuth. (See end of Table IX.)

TABLE XIII.—*Mercury in Bismuth.*

Thermometer, Müller.

Weight of bismuth in block.	Weights of mercury added in succession.	Total weight of mercury in block.	Freezing point of solution.	Atoms of mercury per 100 of bismuth.	Atomic fall.
50			266·65°		
,,	0·108	0·108	266·17	0·225	2·13
,,	0·330	0·439	264·65	0·911	2·20
,,	1·137	1·575	259·77	3·27	2·10
,,	0·494	2·069	257·80	4·29	2·06

CADMIUM AS SOLVENT.

TABLE XIV.—*Sodium in Cadmium.*

Thermometer, Hicks' 15.

Weight of cadmium in block.	Weights of sodium added in succession.	Total weight of sodium in block.	Freezing point of solution.	Atoms of sodium per 100 of cadmium.	Atomic fall.
300			320·41°		
,,	0·355	0·355	317·82	0·577	4·49
,,	0·272	0·627	315·76	1·017	4·57
,,	0·1575	0·785	314·72	1·27	4·48

The molecule in solution apparently contains 1 atom of sodium.

TABLE XV.—*Copper in Cadmium.*

Thermometer, Hicks' 15.

Series I.

Weight of cadmium in block.	Weights of copper added in succession.	Total weight of copper in block.	Freezing point of solution.	Atoms of copper per 100 of cadmium.	Atomic fall.
250			319·77°		
260·4	0·5576	0·5576	318·45	0·38	3·47
270·4	0·623	1·181	317·13	0·775	3·41
280·4	0·675	1·856	315·95	1·173	3·24

Series II.

300			320·26°		
311·5	0·0984	0·0984	320·04	0·056	3·93
317·3	0·1475	0·2459	319·8	0·137	3·36
325·4	0·2192	0·4651	319·35	0·253	3·60
339·0	0·591	1·056	318·25	0·553	3·63
351·5	1·001	2·057	316·56	1·04	3·56
364·0	1·503	3·56	314·1	1·736	3·55
374·27	1·008	4·568	312·86	2·166	3·41
379·27	0·508	5·076	312·88	saturated	

Series III.

300			320·54°		
310	0·1127	0·1127	320·31	0·0646	3·56
320	0·093	0·205	320·14	0·1142	3·50
330	0·521	0·7258	319·12	0·3906	3·63

The alloys were made in a sealed vacuous tube. The copper dissolves at a faint red heat. The alloys have a great surface curvature, and, unlike most cadmium alloys, do not adhere to the glass. Series III was made as a check on the others at a later date, when we were more familiar with the behaviour of cadmium alloys.

TABLE XVI.—*Zinc in Cadmium.*

Series I.

Thermometer, Geissler.

Weight of cadmium in block.	Weights of zinc added in succession.	Total weight of zinc in block.	Freezing point of solution.	Atoms of zinc per 100 of cadmium.	Atomic fall.
101·45			323·4°		
112·00	0·545	0·545	321·07	0·84	2·76
122·0	0·5784	1·1234	319·15	1·585	2·68

Series II.

Thermometer, Hicks' 15.

300			320·27°		
307·2	0·1146	0·1146	320·09	0·0656	2·74

These falls receive a reasonable explanation by the assumption that the body is Cd_xZn_2, *plus* a certain pressure of simpler molecules necessary to maintain equilibrium.

TABLE XVII.—*Arsenic in Cadmium.*

Thermometer, Hicks' 15.

Weight of cadmium in block.	Weights of arsenic added in succession.	Total weight of arsenic in block.	Freezing point of solution.	Atoms of arsenic per 100 of cadmium.	Atomic fall.
300			320·56°		
310	0·1710	0·171	320·2	0·0823	4·37
320	0·2153	0·3863	319·72	0·180	4·67
330	0·1903	0·5766	319·34	0·2606	4·68
340	0·3285	0·9051	319·2	0·397	saturated
360		0·9051	319·2		

The molecule in solution appears to contain 1 atom of arsenic.

TABLE XVIII.—*Palladium in Cadmium.*

Thermometer, Hicks' 15.

Weight of cadmium in block.	Weights of palladium added in succession.	Total weight of palladium in block.	Freezing point of solution.	Atoms of palladium per 100 of cadmium.	Atomic fall.
300			320·45°		
310·3	0·167	0·167	320·3	0·0565	2·65
320·3	0·2155	0·3825	320·16	0·126	2·30
330·3	0·210	0·5925	320·02	0·195	2·24
340·3	0·200	0·7925	319·9	0·26	2·12
355·3	0·500	1·2925	319·82	0·382	saturated
405·3		1·2925	319·82		

TABLE XIX.—*Silver in Cadmium.*

Thermometer, Hicks' 15.

Weight of cadmium in block.	Weights of silver added in succession.	Total weight of silver in block.	Freezing point of solution.	Atoms of silver per 100 of cadmium.	Atomic rise.
300			320·42		
310	0·082	0·082	320·73	0·0275	11·27
320	0·132	0·214	321·17	0·0695	10·79
330	0·110	0·324	321·47	0·102	10·30
340	0·1765	0·5005	321·99	0·1529	10·27

The experiments could not be carried to a higher concentration, because the hard substance which separated endangered the thermometer. It appears probable that the body which separates out is not, as usual, the pure solvent, but is a compound. It follows from the theory that if the body separating out is richer in silver than the solution, the freezing point would rise. We have strong additional evidence, from the behaviour of a triple alloy of silver, cadmium, and lead, of the existence of this compound. The phenomena are comparable to the behaviour of the triple alloy of gold, cadmium, and tin described in a previous paper (Trans., 1891, **59**, 936). We hope shortly to publish the account of this and several other definite compounds detected by the same method.

TABLE XX.—*Tin in Cadmium.*

Thermometer, Geissler.

Weight of cadmium in block.	Weights of tin added in succession.	Total weight of tin in block.	Freezing point of solution.	Atoms of tin per 100 of cadmium.	Atomic fall.
112			323·25°		
,,	0·7816	0·7816	320·15	0·662	4·68
,,	1·16	1·942	315·93	1·644	4·45
,,	1·17	3·112	311·85	2·636	4·33

There appears to be no evidence of combination, and the dissolved molecule is monatomic.

TABLE XXI.—*Antimony in Cadmium.*

Thermometer, Hicks' 15.

Weight of cadmium in block.	Weights of antimony added in succession.	Total weight of antimony in block.	Freezing point of solution.	Atoms of antimony per 100 of cadmium.	Atomic fall.
300			320·49°		
,,	0·266	0·266	320·12	0·080	4·62
,,	0·397	0·664	319·61	0·194	4·54
,,	0·619	1·283	318·82	0·363	4·60

TABLE XXII.—*Platinum in Cadmium.*

Thermometer, Hicks' 15.

Weight of cadmium in block.	Weights of platinum added in succession.	Total weight of platinum in block.	Freezing point of solution.	Atoms of platinum per 100 of cadmium.	Atomic fall.
300			320·4°		
310·7	0·3006	0·3006	320·14	0·0557	4·67
320·7	0·3028	0·6034	319·92	0·1083	4·43
331·3	0·3024	0·9058	319·80	0·1573	saturated

TABLE XXIII.—*Gold in Cadmium.*

Series I.

Thermometer, Hicks' 15.

Weight of cadmium in block.	Weights of gold added in succession.	Total weight of gold in block.	Freezing point of solution.	Atoms of gold per 100 of cadmium.	Atomic fall.
300			320·37°		
310	0·748	0·748	320·18	0·137	1·39
321	0·368	1·116	320·09	0·198	1·41
341	2·918	4·034	319·35	0·682	1·5

Series II.

Thermometer, Hicks' 15.

300			320·65°		
,,	0·570	0·570	320·49	0·108	1·48
,,	0·587	1·157	320·3	0·219	1·6
,,	1·033	2·190	320·0	0·415	1·57
,,	1·056	3·246	319·67	0·615	1·59
,,	1·072	4·318	319·36	0·818	1·58
,,	1·041	5·359	319·04	1·016	1·59
,,	1·805	7·164	318·46	1·358	1·61
,,	2·189	9·354	317·74	1·773	1·64
,,	3·260	12·614	316·67	2·390	1·67
,,	4·135	16·749	315·22	3·174	1·71

Series III,

Obtained with a different thermometer, gave almost identical atomic falls, showing the same tendency for the value of the atomic fall to increase with concentration.

These numbers point to the existence of a molecule $(AuCd)_3$, together with some free atoms of gold, sufficient, with the practically constant mass of cadmium present, to maintain the equilibrium. We have succeeded in obtaining a compound whose percentage composition corresponds to the empirical formula AuCd. The results of these experiments are published in an appendix to this paper.

TABLE XXIV.—*Mercury in Cadmium.*

Thermometer, Hicks' 15.

Weignt of cadmium in in block.	Weights of mercury added in succession.	Total weight of mercury in block.	Freezing point of solution.	Atoms of mercury per 100 of cadmium.	Atomic fall.
300			320·59°		
,,	0·1528	0·1528	320·52	0·0285	2·46
,,	0·4802	0·633	320·3	0·118	2·46
,,	0·7582	1·391	319·92	0·259	2·58
,,	1·742	3·133	319·05	0·584	2·64
,,	2·80	5·933	317·59	1·106	2·71
,,	5·129	11·062	314·93	2·063	2·74
,,	6·57	17·632	311·59	3·288	2·74
,,	11·74	29·372	305·5	5·477	2·76

TABLE XXV.—*Thallium in Cadmium.*

Weight of cadmium in block.	Weights of thallium added in succession.	Total weight of thallium in block.	Freezing point of solution.	Atoms of thallium per 100 of cadmium.	Atomic fall.
300			320·42°		
,,	0·518	0·518	319·98	0·0948	4·64
,,	1·378	1·896	318·84	0·3470	4·55
,,	0·718	2·614	318·23	0·479	4·57
,,	0·922	3·536	317·47	0·647	4·56
,,	7·299	10·835	311·84	1·983	4·33

TABLE XXVI.—*Lead in Cadmium.*

Thermometer, Geissler.

Weight of cadmium in block.	Weights of lead added in succession.	Total weight of lead in block.	Freezing point of solution.	Atoms of lead per 100 of cadmium.	Atomic fall.
112·9			323·0°		
,,	1·742	1·742	319·35	0·837	4·36
,,	1·111	2·853	316·9	1·372	4·45

TABLE XXVII.—*Bismuth in Cadmium.*

Thermometer, Hicks' 15.

Weight of cadmium in block.	Weights of bismuth added in succession.	Total weight of bismuth in block.	Freezing point of solution.	Atoms of bismuth per 100 of cadmium.	Atomic fall.
350			320·28°		
,,	0·349	0·349	320·04	0·0537	4·47
,,	0·468	0·817	319·72	0·126	4·45
,,	0·900	1·717	319·09	0·2644	4·50
,,	1·601	3·318	317·93	0·5109	4·60
,,	2·748	6·066	316·05	0·9341	4·53
,,	10·106	16·172	309·88	2·490	4·18
,,	2·33	18·50	308·56	2·849	4·11
,,	5·46	23·96	305·61	3·690	3·98

LEAD AS SOLVENT.

TABLE XXVIII.—*Sodium in Lead.*

Thermometer, Hicks' 16.

Weight of lead in block.	Weights of sodium added in succession.	Total weight of sodium in block.	Freezing point of solution.	Atoms of sodium per 100 of lead.	Atomic fall.
400			327·5°		
,,	0·41	0·41	326·35	0·92	1·25
,,	0·47	0·88	325·16	1·974	1·19
,,	0·513	1·393	323·88	3·125	1·16
,,	0·602	1·995	322·46	4·475	1·13

TABLE XXIX.—*Magnesium in Lead.*

Thermometer, Müller.

Series I.

Weight of lead in block.	Weights of magnesium added in succession.	Total weight of magnesium in block.	Freezing point of solution.	Atoms of magnesium per 100 of lead.	Atomic fall.
55			326·42°		
65	0·1075	0·1075	320·10	1·404	4·50
Series II.					
55			326·45		
60	0·1015	0·1015	319·80	1·436	4·63

The alloys were made in vacuous hard glass tubes.

The magnesium dissolves in the lead at a red heat, with much incandescence, and reduction of the glass.

The alloys are brittle.

Aluminium in Lead.

Aluminium foil, when heated with lead in a vacuum, melts, and mixes freely at a low red heat, but the resulting alloy, when dissolved in more lead, did not cause a fall in the freezing point.

Ramsay (*System of Inorganic Chemistry*, p. 582) says that aluminium and lead do not alloy. The phenomenon may be analogous to that of thallium in lead (*q.v.*).

TABLE XXX.—*Copper in Lead.*

Thermometer, Müller.

Weight of lead in block.	Weights of copper added in succession.	Total weight of copper in block.	Freezing point of solution.	Atoms of copper per 100 of lead.	Atomic fall.
55			326·47°		
60	0·02	0·02	325·80	0·109	6·15
62	0·017	0·037	325·30	0·195	6·0
67		0·037	325·30	saturated	
77		0·037	325·48	0·157	6·3

Copper dissolves in lead in a vacuum with great ease, but a very small quantity saturates lead at its melting point. Ramsay (*loc. cit.*, p. 587) notes the fact that alloys of copper and lead separate into two layers.

TABLE XXXI.—*Zinc in Lead.*

Thermometer, Hicks' 16.

Weight of lead in block.	Weights of zinc added in succession.	Total weight of zinc in block.	Freezing point of solution.	Atoms of zinc per 100 of lead.	Atomic fall.
380			327·38°		
385	0·312	0·312	326·18	0·256	4·69
395	0·354	0·666	324·79	0·532	4·87
405	0·410	1·076	323·12	0·839	5·08
420	0·434	1·510	321·61	1·136	5·08
435	0·836	2·346	319·00	1·704	4·92
450	0·882	3·228	318·3	2·267	saturated
465	0·583	3·811	318·3	2·589	

TABLE XXXII.—*Arsenic in Lead.*

Thermometer, Hicks' 16.

Series I.

Weight of lead in block.	Weights of arsenic added in succession.	Total weight of arsenic in block.	Freezing point of solution.	Atoms of arsenic per 100 of lead.	Atomic fall.
390			327·2°		
395	0·101	0·101	326·85	0·0708	4·94
405	0·230	0·331	325·85	0·226	5·97
415	0·216	0·547	325·01	0·364	6·02
425	0·266	0·813	324·08	0·528	5·91
440	0·404	1·217	322·81	0·763	5·75
455	0·879	2·096	319·9	1·271	5·74
470	1·468	3·564	315·48	2·092	5·60
490	4·507	8·071	303·46	4·544	5·22
515	7·053	15·124	291·75	8·102	4·38

Series II (made with arsenic resublimed in a vacuum from Na_2CO_3).

370			327·34°		
375	0·514	0·514	325·07	0·378	6·00
385	0·812	1·326	321·70	0·950	5·94
410	6·105	7·431	301·44	5·00	5·18

Inasmuch as the decrease in the atomic fall with increasing concentration is very regular and rapid, the assumption of a gradual polymerisation of the arsenic molecule appears to be admissible.

TABLE XXXIII.—*Palladium in Lead.*

Thermometer, Müller.

Weight of lead in block.	Weights of palladium added in succession.	Total weight of palladium in block.	Freezing point of solution.	Atoms of palladium per 100 of lead.	Atomic fall.
55			326·33°		
60	0·0992	0·0992	324·30	0·323	6·29
62	0·1492	0·2484	321·28	0·782	6·46
64	0·3415	0·5899	314·62	1·799	6·51

The palladium dissolves readily in lead, with slight incandescence.

TABLE XXXIV.—*Silver in Lead.*

Series I.

Thermometer, Müller.

Weight of lead in block.	Weights of silver added in succession.	Total weight of silver in block.	Freezing point of solution.	Atoms of silver per 100 of lead.	Atomic falls.
58			326·22°		
60	0·219	0·219	321·88	0·6996	6·20
70		0·219	322·60	0·5998	6·035
80		0·219	323·16	0·5248	5·83

Series II.

Thermometer, Hicks' 16.

400			327·39°		
,,	0·167	0·167	326·95	0·08	5·5
,,	0·520	0·687	325·42	0·329	5·99
,,	1·204	1·891	321·99	0·903	5·96
,,	2·016	3·907	316·50	1·872	5·82
,,	3·242	7·149	308·46	3·425	5·55
,,	3·291	10·44	302·9	5·00	Sat. { 4·90
,,	2·088	12·528	303·01	6·00	

TABLE XXXV.—*Cadmium in Lead.*

Thermometer, Hicks' 16.

Weight of lead in block.	Weights of cadmium added in succession.	Total weight of cadmium in block.	Freezing point of solution.	Atoms of cadmium per 100 of lead.	Atomic fall.
400			327·38°		
,,	0·1875	0·188	327·04	0·0865	3·93
,,	0·2195	0·407	326·62	0·188	4·05
,,	0·535	0·942	325·60	0·435	4·1
,,	1·008	1·950	323·66	0·900	4·13
,,	2·314	4·264	319·45	1·967	4·03
,,	2·360	6·624	315·31	3·059	3·95
,,	4·010	10·634	308·58	4·906	3·83

TABLE XXXVI.—*Tin in Lead.*

Series I.

Thermometer, Müller.

Weight of lead in block.	Weights of tin added in succession.	Total weight of tin in block.	Freezing point of solution.	Atoms of tin per 100 of lead.	Atomic fall.
60			326·34°		
,,	0·14	0·14	325·55	0·408	1·94
,,	0·136	0·276	324·93	0·804	1·75
,,	0·350	0·626	323·21	1·823	1·72
,,	1·063	2·043	316·97	5·95	1·61
,,	1·024	3·067	312·57	8 93	1·54

Series II.

Thermometer, Hicks' 16.

Weight of lead in block.	Weights of tin added in succession.	Total weight of tin in block.	Freezing point of solution.	Atoms of tin per 100 of lead.	Atomic fall.
400			327·13°		
,,	0·074	0·074	327·08	0·0324	1·64
,,	0·0675	0·1415	327·04	0·0620	1·45
,,	0·4165	0·558	326·66	0·2444	1·93
,,	0·443	1·001	326·35	0·4384	1·78
,,	0·502	1·503	325·96	0·6583	1·78
,,	3·137	4·640	323·66	2·032	1·71
,,	5·151	9·791	320·15	4·289	1·63
,,	13·422	23·213	311·5	10·167	1·54
,,	13·922	37·135	303·46	16·265	1·46
,,	5·015	42·15	300·8	18·462	1·43
,,	16·089	58·239	293·00	25·508	1·34
,,	16·672	74·911	285·87	32·811	1·26

These numbers are consistent with the existence of a molecule Pb_2Sn_4, in equilibrium with free Sn and Pb.

TABLE XXXVII.—*Antimony in Lead.*

Thermometer, Müller.

Weight of lead in block.	Weights of antimony added in succession.	Total weight of antimony in block.	Freezing point of solution.	Atoms of antimony per 100 of lead.	Atomic fall.
55			326·28°		
60	0·217	0·217	323·8	0·622	3·98
62	0·368	0·585	319·91	1·623	3·92
64	0·28	0·865	317·2	2 325	3·9
68	0·9925	1·858	308·22	4·70	3·74

The antimony was a pure sample from tartar emetic.

TABLE XXXVIII.—*Platinum in Lead.*

Thermometer, Müller.

Weight of lead in block.	Weights of platinum added in succession.	Total weight of platinum in block.	Freezing point of solution.	Atoms of platinum per 100 of lead.	Atomic fall.
60			326·16°		
62	0·0865	0·0865	325·21	0·148	6·42
64	0·0935	0·18	324·21	0·299	6·5
66	0·09	0·27	323·38	0·436	6·38
68	0·1134	0·3834	322·38	0·6	6·3

TABLE XXXIX.—*Gold in Lead.*

Series I.

Thermometer, Müller.

Weight of lead in block.	Weights of gold added in succession.	Total weight of gold in block.	Freezing point of solution.	Atoms of gold per 100 of lead.	Atomic fall.
53			326·41°		
,,	0·192	0·192	323·93	0·38	6·52
,,	0·195	0·387	321·75	0·766	6·1
,,	5·13	0·9	315·55	1·78	6·1
,,	5·21	1·421	309·03	2·81	6·2

Series II.

Thermometer, Hicks' 16.

400			327·42°		
,,	0·322	0·322	326·86	0·0845	6·63
,,	0·310	0·632	326·34	0·1658	6·51
,,	1·11	1·742	324·50	0·4568	6·39
,,	3·675	5·417	318·30	1·421	6·42
,,	4·034	9·451	311·44	2·479	6·48
,,	3·102	12·553	306·26	3·292	6·43
,,	2·698	15·251	301·67	4·00	6·44

Series II was carried out with purer gold than Series I. As in the case with other gold alloys, there is a marked constancy, and even a tendency to rise, visible when the atomic falls are plotted.

TABLE XL.—*Mercury in Lead.*

Thermometer, Müller.

Weight of lead in block.	Weights of mercury added in succession.	Total weight of mercury in block.	Freezing point of solution.	Atoms of mercury per 100 of lead.	Atomic fall.
60			326·38°		
,,	0·424	0·424	323·89	0·729	3·41
,,	1·489	1·913	315·48	3·29	3·31
,,	2·007	3·920	304·69	6·74	3·21

These numbers point to a molecule containing Hg_2, and the slow rate of decrease in the atomic falls may indicate union with the lead.

Thallium in Lead.

Considerable quantities of thallium were at different times alloyed with lead, but no change in the freezing point could be detected.

TABLE XLI.—*Bismuth in Lead.*

Thermometer, Müller.

Weight of lead in block.	Weights of bismuth added in succession.	Total weight of bismuth in block.	Freezing point of solution.	Atoms of bismuth per 100 of lead.	Atomic fall.
70			326·34°		
,,	0·163	0·163	325·63	0·229	3·1
,,	0·238	0·401	324·63	0·563	3·04
,,	0·536	0·937	322·35	1·32	3·02
,,	0·744	1·681	319·2	2·36	3·02
,,	1·024	2·705	314·95	3·8	2·99
,,	0·592	3·297	312·61	4·63	2·96

It may be noted that although the concentration in the last experiment is twenty times that of the first, there is practically no decrease in the atomic fall. Hence in this case there is no condensation of the dissolved molecule, but the numbers agree with the hypothesis that a body Pb_xBi_2, or perhaps only Bi_2, is formed. (See also Table XXXVI, Tin in Lead.)

TABLE XLII.—*Showing* approximate *Atomic Fall of different Solvents for Concentrations of about* 1 *atom per* 100.

Metal dissolved.	Solvent.				
	Sodium.	Cadmium.	Tin.	Lead.	Bismuth.
A, *vide* Note II		4·5	3·0	6·5	2·08
B, *vide* Note II		37·43	25·6	27·2	20·88
Lithium	1·2				
Sodium	..	4·5	2·8	1·2	2·0
Magnesium	..	..	2·8	4 6	
Aluminium	..	..	1·3		
Potassium	3·6				
Calcium	..	..	2·4		
Nickel	..	..	2·9		
Copper	..	3·6	2·9	6·3	1·2
Zinc	..	2·7	2·6	5·1	1·5
Arsenic	..	4·7	..	5·9	0·8
Silver	..	*Rise* **10·3**	2·9	6·0	2·0
Palladium	..	2·2	2·8	6·5	2·0
Cadmium	3·4	..	2 4	4·1	2·0
Indium	3·6	..	1·9		
Tin	..	4·6	..	1·7	2·1
Antimony	..	4·6	*Rise* **2·4**	3·9	*Rise* **3·0**
Gold	4·5	1·6	2·9	6·4	2·1
Platinum	..	4·5	..	6·4	2·1
Mercury	4·5	2·7	2·4	3·4	2·2
Thallium	4·2	4·5	2·9	No effect	2·0
Lead	..	4·4	2·8	..	2·1
Bismuth	..	4·5	2·4	3·0	

Note I.—In several cases a concentration of 1 atom per 100 atoms was not reached.

Note II.—The horizontal row of numbers marked A gives the fall calculated from Van't Hoff's theory for a concentration of 1 mol. of dissolved metal in 100 atoms of solvent (for calculation see Trans., 1890, **57**, 390). The row marked B gives the corresponding osmotic pressure in *atmospheres.* The latent heats necessary for calculating the numbers in row A were taken from Person's values as given by Landolt. G. Tammann was unable to find any recorded values of the latent heat of sodium, but gives a value determined by himself which points to a tetratomic molecule for metals dissolved in sodium, but the subject perhaps requires further investigation.

APPENDIX.

From the foregoing tables it will be seen that three different effects may follow from alloying metals with one another.

A. The freezing point is lowered, as in most of the cases we have observed.

B. The freezing point is raised, *e.g.*, silver in cadmium, antimony in tin, antimony in bismuth.

C. The freezing point is unaffected, *e.g.*, thallium in lead, aluminium in lead (?), &c.

In order to show that Van't Hoff's theory is sufficient to explain each of these cases, we have taken a typical example of each, and examined the *solid* and *fluid* part* of the alloy by analysis.

A. *Analysis of a Gold-Lead Alloy.*

To show that in the case where a fall in the freezing point is produced, the first portions of the alloy which solidify are poorer in the dissolved metal than in the fluid part, we made experiments on an alloy of lead and gold.

For this purpose we melted under paraffin 147 grams of pure assay lead foil, and added 3 grams of precipitated gold; the solution was then stirred in one of the iron blocks until it just began to solidify. The alloy was then poured out on to a hot iron wire gauze, which retained the solid part.

The solid part weighed 91 grams, and the fluid part, which ran through the strainer, 54 grams. These two portions were then separately melted up, stirred, and allowed to solidify rapidly so as to get them uniform. The gold was determined by crystallisation in the usual way.

Gold-Lead Alloy.

	Fluid Part.	Solid Part.
Exp. I.	3·090 alloy gave 0·07 Au = 2·26 per cent.	5·574 alloy gave 0·096 Au = 1·72 per cent. Au.
II.	7·002 alloy gave 0·1575 Au = 2·25 per cent.	6·507 alloy gave 0·113 Au = 1·74 per cent. Au.

Hence it is seen that the fluid part contains much more gold than the solid part.

By this method of experimenting it is obvious that it is impossible to obtain pure lead free from the adhering mother liquor. The practical method of obtaining silver from lead by Pattinson's method is an illustration of the same principle. Roberts-Austen (*Introduction to Metallurgy*, p. 61, *et seq.*) has given several beautiful examples of the same kind.

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* By the *solid* part we mean the first portion of the alloy to solidify, and by the *fluid* part the later portion to solidify.

B. *Analyses of a Silver-Cadmium Alloy.*

Since alloys of silver and cadmium freeze at a higher temperature than pure cadmium, it ought to follow from Van't Hoff's theory that the portion solidifying first contains *more silver than* the more fusible part. So that by the crystallisation of the first portion the osmotic pressure in the liquid is *decreased* instead of being increased, as in the usual case.

To test this, an alloy containing 141·76 grams of cadmium and 2·441 grams silver was made, and after complete fusion and thorough stirring, was allowed to cool slowly until a considerable portion was solid. An attempt was then made to pour the liquid part through fine iron wire gauze, but the alloy was too cold, and only 0·947 gram ran through the gauze. This fluid part was labelled A_1.

The mass of crystals and mother liquor lying on the wire gauze, and labelled B_1, was remelted and treated as before by pouring on to the wire gauze. This gave a fluid part of about 25 grams, labelled A_2, that ran through the gauze, and a solid part, labelled B_2.

In addition to the above a portion of solid, weighing 10·04 grams, collected on the stirrer, labelled B'_2. A fragment of B_2, weighing 8·888 grams, was reserved for analysis, and the rest melted for a third time and separated by means of the gauze, giving a solid part B_2 of 81·2 grams, and a fluid part A_3 of 7·47 grams.

In order to analyse the alloys, they were dissolved in nitric acid, and the percentage of silver in them determined by standard ammonium sulphocyanate. The results are given in the following table. The original alloy contained 1·69 per cent. of silver.

A_1	0·74 per cent.	A_2	1·09 per cent.	A_3	1·14 per cent.
B_1	—	B_2	1·77 ,,	B_3.	1·94 ,,
		B'_2	1·63 ,,		

Thus it is clear that if in addition we could allow for the mother liquor adhering to the crystals in B_2, B'_2, and B_3, the solid parts would be found much richer in silver than the original alloy.

This result is exactly in accordance with what theory leads us to expect, and contains the explanation of those abnormal cases in which a binary alloy has a higher freezing point than the pure solvent metal.*

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* Bijlert (*loc. cit.*) has examined the analogous case of antimony in tin by a more elaborate method, and arrived at the same results.

C. *Analysis of a Lead-Thallium Alloy.*

An alloy of lead and thallium was made in a vacuous tube, and allowed to rest at one end of the tube until a portion had solidified; the liquid part was then poured to the other end of the tube and also allowed to solidify. The two parts were very different in appearance, that which solidified first being a hollow shell with a crystalline interior, whilst the part which had been poured off resembled an ordinary lump of lead. On analysis, these two parts proved to be identical in composition.

Result of analysis of solid and fluid part of the above described thallium-lead alloy—

Solid portion..........	17·69	per cent.	thallium.
Fluid portion	17·67	,,	,,

It is thus seen that when an alloy of thallium and lead solidifies there is no separation whatever of the constituents.

The estimation of the thallium in the alloys was made by means of standard permanganate by the method laid down by Crookes, in his "Select Methods of Analysis."* For this purpose the alloys were dissolved in nitric acid, and the solution evaporated down with sulphuric acid; the mixed lead and thallic sulphate were made up to a litre. Portions of 100 c.c. were reduced with SO_2, and boiled; hydrochloric acid was then added, and the titration made with N/50 permanganate in the nearly boiling solution. If the permanganate is of the strength stated above, and the solution is not too acid with hydrochloric acid, the results are very sharp. The method was confirmed by blank experiments on weighed quantities of thallium with lead. We propose to analyse other alloys of lead and thallium in order to confirm this result.

Sidney Sussex College, Cambridge.

LXXVII.—*Isolation of a Compound of Gold and Cadmium.*

By C. T. Heycock, M.A., and F. H. Neville, M.A.

The experiments made by us on triple alloys of gold, cadmium, and tin, described in the Transactions of the Chemical Society, 1891, pp. 936—966, led to the conclusion that a definite compound of cadmium and gold was formed.

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* We must here express our best thanks to Mr. C. T. R. Wilson, B.A., of Sidney College, for carrying out this part of the work.

By the method we then adopted, we were unable to obtain this compound free from the mother liquor from which it was produced. We have since been able to obtain this compound, and, after several trials, we found the following method to give the best results.

A tube of the hardest combustion glass, about 6 in. in length, was sealed at one end, and bent in the middle at a very obtuse angle; in this sealed end was placed a weighed quantity of pure precipitated gold, together with a large excess of cadmium (three or four times the weight of cadmium required). The open end of the tube was then drawn off to a narrow neck, and the tube carefully exhausted with a Sprengel mercury pump, and sealed off. In order to ensure success, it is necessary that the vacuum should be a very good one, such as is obtained by putting sulphuric acid on the top of the mercury in the pump. When complete, the tube resembled a Faraday's tube for the liquefaction of gases, except that the bend was only just perceptible. The tube was then arranged in a combustion furnace in such a way as to allow the cadmium to condense and run away from the alloy. After the cadmium was melted, the tube was thoroughly shaken to mix the cadmium with the gold. The moment of combination and solution was marked by a fairly bright incandescence of the gold. The end of the tube with the charge was then heated for five or six hours to a temperature about that at which the glass began to be pressed in, when the excess of cadmium slowly and regularly distilled off, until towards the close of the process no further condensation was apparent.

The gold in the alloy was determined by digestion with successive quantities of nitric acid for some hours.

Exp. I. Five grams of precipitated gold was sealed up with about 14 grams of cadmium. After distilling off the excess of cadmium for two hours, the resulting alloy was found to weigh 8·003 grams. This alloy was broken into two parts; one part, weighing 2·936 grams, gave 1·83 grams of gold = 62·33 per cent. Au.

Exp. II. The other part of the above alloy, weighing 5·026 grams, was again sealed in a vacuous tube, and *redistilled* for two hours, when a little cadmium passed over; the resulting alloy weighed 4·779 grams, and yielded 3·1405 grams of gold = 65·7 per cent. Au.

Exp. III. Five grams of gold and 20 grams of cadmium, after distilling for six hours, gave an alloy weighing 7·841 grams.

A portion of this alloy, weighing 3·4995 grams, gave 2·372 grams of gold = 63·92 per cent. Au.

Hence the three fairly concordant experiments gave a mean value for the percentage of gold in the compound = 63·98, which corresponds to the empirical formula AuCd.

Per cent. Au found.	Per cent. Au calculated for AuCd.
63·98	63·71

The alloy of cadmium and gold is of a greyish and silvery white appearance, somewhat like cadmium. It is very brittle, and has a highly crystalline fracture. It is scarcely attacked by cold nitric acid (1 acid to 1 water), but is readily acted on by hot nitric acid, or hot hydrochloric acid, leaving the gold in the shape of the original ingot.

The immediate interest of this compound, for us, is that it confirms the supposition we brought forward last summer to account for the remarkable behaviour of gold and cadmium when dissolved in tin.

We have not at present been able to prepare a compound richer in cadmium than AuCd, although our previous experiments gave strong indications that such a body exists.

Sidney Sussex College Laboratory,
Cambridge.

LXXVIII.—*The Resins of Ficus rubiginosa and Ficus macrophylla.* (Preliminary Notice.)

By Edward H. Rennie, D.Sc. (Lond.), Professor of Chemistry in the University of Adelaide, and G. Goyder, Jun.

In the year 1859, De la Rue and Müller communicated a paper to the Royal Society (*Phil. Trans.*, 1860, 43), in which they described the results of an examination of the resin of *Ficus rubiginosa*. A sample of this resin, which had been sent to the Paris Exhibition of 1855, was brought under their notice by Sir Wm. McArthur. They separated from it:—(1) a resinous portion readily soluble in cold alcohol (73 per cent.); (2) a white, crystalline portion, readily soluble in warm alcohol (14 per cent.); and (3) caoutchouc, &c. (13 per cent.). The resinous portion soluble in cold alcohol was but little investigated, owing to difficulties met with in attempts to purify it. The crystalline material yielded two substances, one in very small quantity (too small for detailed examination), and a second in comparatively large quantity, which was found to contain

Carbon	79·11	and	79·08	per cent.
Hydrogen	10·23	„	10·34	„

The formula $C_{20}H_{16}O_2$ (old notation) was therefore ascribed to it, and it was named sycoceryl acetate, because on hydrolysis it yielded acetic acid and an alcohol to which the name sycoceryl alcohol was given. In order to obtain the acetate pure, De la Rue and Müller first repeatedly crystallised their material from hot alcohol, then they partially dissolved it in ether at 30°, and, having allowed the ethereal solution to cool, filtered off a small quantity of flocculent matter (the other crystalline substance above referred to as present in small quantity). On distilling off the ether, crystals were obtained which were apparently pure. These crystals were very similar to those of cholesterol, and melted at from 118° to 120°. On hydrolysis, the substance yielded acetic acid, and an alcohol which was purified simply by recrystallisation from warm alcohol. It is described as melting at about 90°, and as crystallising in spherical masses resembling wavellite. The numbers obtained on combustion were as follows:—

Carbon	82·94	and	81·85	per cent.
Hydrogen	11·57	„	11·20	„

De la Rue and Müller state, however, that on one occasion they obtained on hydrolysis a substance closely resembling that just described, but giving on combustion

Carbon	84·81	and	84·50	per cent.
Hydrogen	11·76	„	11·87	„

and they suggest that this may be the ether corresponding to the alcohol.

It has been thought necessary to give this brief *résumé* of the work of De la Rue and Müller for the sake of comparison with the results obtained by us in the examination of very similar products.

Some three years ago, through the kindness of Mr. J. H. Maiden, Curator of the Technological Museum in Sydney, one of us received a small quantity of the liquid which exudes from *Ficus rubiginosa* when the tree is punctured or wounded. After evaporation on the water-bath, an excessively sticky mass remained, which looked very unpromising. It yielded some soluble matter to alcohol, and was finally extracted thoroughly with boiling alcohol, leaving a residue resembling caoutchouc, which was not further examined. The alcoholic extract did not deposit any crystalline matter on cooling, but, on dilution or evaporation, a nearly white substance was obtained, from which, so far as the experiments went, no crystalline substance could be separated. It was therefore boiled with alcoholic potash; on dilution, a white substance separated, which, to all outward appearance, was the same as the original, and showed no signs of crystallisation. The alkali solution, however, was found to yield, on acidification, a small quantity of *cinnamic acid*, which was identified by its actions and melting point. An ethereal extract of the *alkaline* solution, after boiling off the alcohol, and subsequent evaporation, left a residue with a distinct smell of hyacinths. Possibly, therefore, traces of cinnamic alcohol had been formed during hydrolysis, but if so there was not sufficient for identification. The juice obtained from *Ficus rubiginosa*, therefore, if it contain the crystalline substances above described, does not readily yield them in a crystalline form. Possibly a more careful examination would give more satisfactory results, but as a quantity of the *dried* resin came to hand and promised much better results, our attention was directed to it.

We are indebted to Mr. Maiden also for a supply of the dried resin both of *Ficus rubiginosa* and *Ficus macrophylla*. We first directed our attention to the former. A preliminary experiment having convinced us that crystalline substances were present, the resin was extracted with boiling strong alcohol till nothing more could be dissolved. The residue consisted of a substance resembling caoutchouc (not further examined), fragments of bark, &c. The alcoholic extracts, on cooling, deposited impure crystals, which were then repeatedly crystallised from boiling alcohol. The second crystalline substance described by De la Rue and Müller as obstinately adhering to the sycoceryl acetate was not observed by us, nor, on dissolving in ether at 30° as recommended by them, did any flocculent substance separate as the ether cooled. In fact, by repeated crystallisation from boiling alcohol, a substance was obtained which appeared homogeneous under the microscope, and the melting point of which seemed to be constant after further crystallisation. In order to determine the melting point, the purified crystals were crystallised twice more from boiling alcohol (nearly absolute). They then melted at 120—121°. After a third crystallisation from the same medium, the melting point remained the same. The substance thus obtained exhibited the closest external resemblance to the sycoceryl acetate described by De la Rue and Müller, except that the melting point found by us was slightly higher than that given by them. It formed shining plates, often six-sided, and much resembled cholesterol in appearance.

An examination of the resin from *F. macrophylla* gave precisely similar results in so far as this crystalline substance was concerned, but no comparison has yet been made between the two samples of resin to ascertain whether or not there are other differences. The crystalline substance obtained from *F. macrophylla* was shown to be identical with that from *F. rubiginosa*, by its appearance, melting point, reactions, and analysis.

On submitting it to combustion, however, numbers were obtained which differed very considerably from those obtained by De la Rue and Müller. Our numbers lead to the formula $C_{34}H_{56}O_2$, a result which is confirmed by experiments to be presently described.

	Theory for		From *F. rubiginosa.*	
	$C_{34}H_{56}O_2$.	$C_{34}H_{54}O_2$.	I.	II.
Carbon*	82·26	82·59	82·04	81·64
Hydrogen	11·29	10·93	11·63	11·45
Oxygen	6·45	6·48	—	—
	100·00	100·00		

	From *F. macrophylla.*				
	III.	IV.	V.	VI.	VII.
Carbon*........	81·85	81·81	82·24	82·15	82 02
Hydrogen	11·54	lost	11·20	11·25	11·50
Oxygen	—	—	—	—	—

It will be seen that the figures for carbon are about 3 per cent., and those for hydrogen about 1 per cent. higher than those obtained by De la Rue and Müller for the substance they examined. Of course, the numbers do not definitely decide between the alternative formulæ given by us, but as far as they go they favour the formula $C_{34}H_{56}O_2$, and this formula is further confirmed by the results of the combustions of the alcohol obtained by hydrolysis.

On warming with alcoholic potash or soda, the compound was readily hydrolysed, and the liquid, on cooling, deposited another substance, which crystallised in spherical masses of needles, just as described by De la Rue and Müller, acetic acid being formed at the same time. The crystalline mass was filtered off and recrystallised several times from very strong alcohol; in fact, till the melting point was not altered by further crystallisation. It then melted at 114°, a temperature considerably higher than that given for the substance obtained by De la Rue and Müller (about 90°). On combustion, it gave results differing considerably from those first obtained by the authors just named, but agreeing fairly well with those given by a substance which they obtained on one occasion by hydrolysis (*vide supra*). The following are the numbers :—

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* It is usual to give the actual analytical figures in these cases, but in the present instance the paper was written during a holiday at a distance from Adelaide, and in the notes hastily written down for the purpose from the note-books, it happened that only the results were transcribed. The same remark applies to the combustion of sycocerylic alcohol given further on in the paper.—E. H. R.

	Theory for				
	$C_{32}H_{54}O$.	$C_{32}H_{52}O$.	I.	II.	III.
Carbon	84·58	84·95	84·67	84·45	84·20
Hydrogen	11·89	11·50	12·11	12·03	11·98
Oxygen	3·53	3·55	—	—	—
	100·00	100·00			

These figures favour the formula $C_{32}H_{54}O$ rather than the other, and therefore so far confirm the formula $C_{34}H_{56}O_2$ for the acetate.

In order to ascertain whether acetic acid was formed during hydrolysis, a portion of the original substance was warmed with alcoholic soda, the alcohol distilled off, the residual liquor filtered, and the filtrate acidified with pure sulphuric acid and distilled. The distillate, on neutralisation with barium carbonate, yielded a soluble barium salt which behaved as barium acetate, and was analysed with the following result:—

0·5045 gram of substance gave 0·4645 gram $BaSO_4$ = 0·27312 gram of barium = 54·13 per cent.

Theory for $Ba(C_2H_3O_2)_2$ ...... 53·72 per cent.

A weighed portion of the acetate was then taken and hydrolysed as above, but the crystalline substance was carefully extracted (after distilling off the alcohol) by ether, the ethereal solution put into a weighed flask, and the ether distilled off. The residue was first dried as far as possible at 100°, then just melted, air being gently blown into the flask till it no longer lost weight. The following are the figures:—

3·8844 grams of the acetate gave 3·6045 grams of the product of hydrolysis = 92·8 per cent.

The equation

$$C_{34}H_{56}O_2 + NaOH = C_{32}H_{54}O + CH_3{\cdot}COONa$$

requires 91·53 per cent., a very fair result, considering the difficulties of the operation. A similar equation for substances having the compositions of those examined by De la Rue and Müller would require 86·18 per cent.

Molecular weight determinations of the product of hydrolysis were then made by Raoult's freezing point method. The following are the details, acetic acid being used as the solvent:—

I. Weight of substance taken .. 0·1725 gram.
" solvent " .. 24·033 grams.

Freezing point of solvent (arbitrary scale)	1·443°
,, ,, solution ,,	1·377°
Actual depression of freezing point	0·063°

Therefore, using the constant 3860 given by Ostwald for acetic acid—

$$\text{Molecular weight} = \frac{3860 \times 0{\cdot}1725}{0{\cdot}063 \times 24{\cdot}033} = 439.$$

II. Weight of substance taken ..	0·175 gram.
,, solvent ,, ..	23·595 grams.

Freezing point of solvent (arbitrary scale)	2·660°
,, ,, solution ,,	2·592°
Actual depression of freezing point	0·068°

Therefore, as above, molecular weight

$$= \frac{3860 \times 0{\cdot}175}{0{\cdot}068 \times 23{\cdot}595} = 421.$$

These figures come very fairly near that calculated for the formula $C_{32}H_{54}O$, namely 454, considering that a difference of 0·01° would make a difference of about 70 in the molecular weight. The formula for the substance described by De la Rue and Müller, $C_{16}H_{30}O$, would require a molecular weight of 262.

We propose to submit these substances to a closer examination, and to study their oxidation products. Experiments are now in progress having these objects in view.

The mother liquors from the earlier crystallisations of the acetate deposited on standing an apparently amorphous substance, also some long needles. These substances have not yet been examined.

LXXIX.—*Fluosulphonic Acid.*

By T. E. Thorpe, F.R.S., and Walter Kirman, Assoc. Roy. Coll. Science, South Kensington.

Liquid hydrogen fluoride, as Gore has shown, acts with great violence upon liquid sulphur trioxide; when care is taken to mix the two substances in the proper proportions, and at as low a temperature as possible, we find that the product is a mobile, colourless liquid, which comports itself like the chlorosulphonic acid discovered by Williamson, and which therefore may be conveniently termed *fluosulphonic acid.*

In order to prepare fluosulphonic acid, we made use of the platinum apparatus already employed by one of us, in conjunction with Mr. F. J. Hambly, in the preparation of the liquid hydrogen fluoride required for the experiments on the vapour density of this substance (Trans., 1889, **55**, 163). A quantity of sulphur trioxide, obtained by gently heating a mixture of sulphuric anhydride (procured from Messrs. Chapman and Messel) and phosphoric oxide, was distilled into the receiver, the weight of which was known. After again weighing, by which the amount of sulphur trioxide present was ascertained, the receiver was connected with the retort in which was heated a quantity of the double fluoride of hydrogen and potassium. The condensing tube and receiver were cooled by a mixture of ice and calcium chloride. The double fluoride was used in such quantity that the presence in the receiver of an excess of hydrogen fluoride, over and above the amount needed to form the compound $SO_2(OH)F$, could be ensured, as demonstrated by again weighing the receiver. In order to remove the uncombined hydrogen fluoride, the receiver and its contents were heated to a temperature between 25° and 35°, and a stream of dry carbon dioxide was passed through the liquid. In one of the preparations a sample weighing about 60 grams lost in weight by this treatment as follows:—After $4\frac{1}{2}$ hours, 2·1 grams; after 6 hours more, 0·85 gram; after 2 hours further treatment, 0·4 gram; and after 6 hours additional treatment, during which time the current of carbon dioxide was occasionally very rapid, 1·5 grams. A portion of this loss, especially at the later stages, is doubtless due as much to the volatilisation of the fluosulphonic acid as to the dissipation of any dissolved hydrogen fluoride. After the second period, an analysis of the liquid showed that the ratio of SO_3 to HF was 1 to 1·15. After the last period, the mean of two concordant analyses gave the ratio 1 to 1·13.

The analysis of fluosulphonic acid is attended with some little difficulty, owing to the extraordinary energy with which the substance reacts with water; the decomposition, indeed, is almost explosive in violence. The best method of operating we found to be as follows:—About 1 c.c. of the liquid was poured into a small platinum tube, which was allowed to slide into distilled water, contained in a platinum bottle of such dimensions that the water did not come in contact with the liquid so long as the bottle remained vertical. The bottle was then tightly closed by means of a caoutchouc stopper, and surrounded by ice. After some time the bottle was carefully tilted in such a manner that the liquids were caused to mix. After the violent reaction was at an end, and after standing for some time, the solution was poured into a platinum dish, and its acidity determined by titration with a standard solution of pure soda, after which the sulphuric acid was precipitated by the addition of barium chloride and hydrochloric acid. The barium sulphate after weighing was tested for any admixed fluoride; if present, its amount was determined by heating with pure sulphuric acid, igniting, and again weighing. The increase in weight was due to the conversion of BaF_2 into $BaSO_4$, so that by subtracting the weight of BaF_2 equivalent to this change from the first weight of the precipitate, the real amount of $BaSO_4$ was obtained, and hence the amount of SO_3. The total acidity of the solution was determined in terms of SO_3; the difference gave the SO_3 equivalent of the hydrofluoric acid. The amount of barium fluoride precipitated with the barium sulphate varied between 0·8 and 1·5 per cent. of the weight of the precipitate.

The results of an analysis made by this method gave—

SO_3	1·0891 grams.
HF	0·3053 „

Or 1 mol. SO_3 to 1·11 mols. HF.

Of a later preparation two analyses gave—

SO_3	0·8797 gram.	0·7871 gram,
HF	0·2516 „	0·2196 „

being in the proportion of 1 mol. SO_3 to 1·14 and 1·12 mols. HF respectively.

In order to determine the boiling point of the fluosulphonic acid, a small platinum retort was fitted to the condensing tube of the hydrofluoric acid apparatus. The retort was provided with a neck into which was ground a thin platinum tube closed at the bottom, to serve as a case for the thermometer. When distilling water in this apparatus, the thermometer used indicated 99·3° under a barometric pressure of 764·6 at 17°. As the true boiling point of water under these conditions is 100·2°, the correction was +0·9. About 30 grams of fluosulphonic acid was poured into the retort, and carefully heated. The temperature, as read from the thermometer, rose rapidly to 158°, and then slowly increased to 160°, at which temperature almost the whole of the liquid distilled over. The results of four different distillations corrected for scale error and emergent column gave—

(1) 163·3°; (2) 162·3°; (3) 162·0°; (4) 162·9°.

Hence the boiling point of fluosulphonic acid may be taken without sensible error as 162·6°, the mean value of the foregoing determinations.

In reality fluosulphonic acid, like chlorosulphonic acid, cannot be distilled without more or less decomposition. It then in all probability forms a greater or less quantity of sulphuryl difluoride, analogous to the sulphuryl dichloride obtained by Behrend by heating chlorosulphonic acid under pressure—

$$2SO_2{\cdot}O{\cdot}HF = SO_2F_2 + SO_4H_2.$$

The evidence for this supposition is furnished by the facts that the ratio of HF to the SO_3 in the distillate is continually increased by successive distillations, and that there is invariably a residue of sulphuric acid left in the retort at the conclusion of the operation. SO_2F_2 on decomposition by water would, of course, yield the ratio $1SO_3$ to 2HF.

Thus, after expulsion of excess of HF by dry carbon dioxide, the ratio of SO_3 to HF was 1 to 1·1; after several distillations, the ratio was 1 to 1·37. In a second series of observations, the ratio of SO_3 to HF before distillation was 1 to 1·13; after distillation it was 1 to 1·32 and 1·30 (2 analyses). The redistilled liquid was found to pass over at 163·6, which is but slightly higher than the mean of the several boiling points given above.

We have little doubt that sulphuryl difluoride might be readily obtained by Behrend's method; that is, by heating fluosulphonic acid in a sealed platinum vessel to a sufficiently high temperature.

Fluosulphonic acid is a thin, colourless liquid, which fumes in the air, and boils with slight decomposition at 162·6°. It has a faint, pungent smell, and has but little action on the dry skin; it feels greasy to the touch, and is without the intense blistering action of hydrogen fluoride. It slowly attacks glass, more rapidly in presence of moist air; it quickly acts on lead, forming lead sulphate and fluoride.

It is noteworthy that fluosulphonic acid boils at a considerably higher temperature than its analogue chlorosulphonic acid, the boiling point of which was found by one of us (Thorpe, Trans., 1880, **37**, 358) to be 155·3°. This fact is possibly connected with the relatively high boiling point of hydrogen fluoride as compared with that of hydrogen chloride.

LXXX.—*Note on the Interaction of Iodine and Potassium Chlorate.*

By T. E. THORPE, F.R.S., and GEORGE H. PERRY, Assoc. Roy. Coll. Science.

THE interaction of iodine and potassium chlorate, first employed by Berzelius for the preparation of iodine monochloride, is usually represented by the equation

$$3KClO_3 + I_2 = KClO_4 + KCl + KIO_3 + ICl + O_2.$$

We find, however, that when an intimate mixture of iodine and potassium chlorate, in the proportions demanded by the above equation, is heated, not only is the yield of iodine monochloride invariably very far below the theoretical amount, but that much of what actually is formed is converted into the solid trichloride, and that free chlorine and more or less iodic anhydride are often simultaneously formed. These facts seem to show that the actual change is very imperfectly indicated by the equation above given.

Careful quantitative experiments, so arranged that the various products of the change, both fixed and volatile, could be estimated, have shown that, in reality, the primary and main reaction between iodine and potassium chlorate is a simple metathesis:—

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2.$$

The chlorine so liberated attacks any iodine that is not within the "sphere of action" of the heated chlorate, and forms more or less mono- and tri-chloride of iodine, in amounts depending upon the temperature and mode of heating. When care is taken not to heat the mixture to a higher temperature than is actually necessary to effect the above change, the saline residue contains only traces of potassium chloride and perchlorate, which seems to indicate that these substances are not really products of the direct action, but are formed by local superheating of the chlorate, with evolution, of course, of oxygen, and consequent formation of iodine pentoxide. By careful management, it is possible to convert practically the whole of the iodine present into potassium iodate, with the liberation of the equivalent amount of gaseous chlorine.

Iodine monochloride, as is well known, is readily dissociated by heat into the trichloride and free iodine. It seemed to us interesting to determine whether a solution of iodine monochloride in chloroform or carbon tetrachloride would show any indication of such dissociation when allowed to diffuse into a quantity of the same solvent.

The experiment indicated that no such dissociation occurred, but that the ratio of iodine to chlorine remained unchanged throughout the mass of the solution, a conclusion in harmony with the results of recent work by Stortenbeker (*Zeit. physikal. Chem.*, **10**, 183).

LXXXI.—*The Hydrolytic Functions of Yeast.* Part II.

By JAMES O'SULLIVAN.

HAVING satisfied myself by numerous experiments, besides those given in Part I (this vol., p. 593), that invertase does not leave the healthy yeast cell when the latter inverts cane sugar under the conditions therein mentioned, I proceeded to determine whether the velocity of the hydrolytic action followed the same course as that of sulphuric acid on cane sugar (Wilhelmy and Ostwald), or that of invertase, under the most favourable conditions (O'Sullivan and F. W. Tompson, Trans., 1890, **57**, 865).

What urged me to investigate this question was the conception that, as the action of acid and of invertase on cane sugar complies with "Harcourt's law," each individual active living yeast cell, capable of producing alcoholic fermentation, might be considered as comparable with a "chemical molecule," so far as its hydrolytic action was concerned.

It has been mathematically shown that when a simple chemical change takes place, there is a constant, or an invariable number, to be obtained from the amount of the changing substance at the beginning of the reaction and the time taken to alter any fraction of that substance. The value of this constant K is deduced from $\frac{1}{\theta}\log\frac{1}{1-x}$, in which θ represents the time in minutes of the duration of the reaction, and x the fraction of the total substance at the start of the reaction, which is altered in the time.

The values of K obtained at various stages, or times, of any one transformation should be constant, if the change follows the course of the above law.

The experiments, the results of which are given in Table I, will, I think, speak for themselves as to the course of the hydrolytic action of yeast being in accord with that of a "simple chemical change."

Mode of Procedure.

Since the hydrolytic action of yeast is solely due to the plasma within the yeast cell, it is at once evident that, if a quantitative expression for that action is sought for, some means must be adopted to keep the yeast in suspension during the progress of the change. In order to do this, I passed a strong current of air through the solutions undergoing hydrolysis, and it will be seen from the following experiments that this aëration had no other influence on the rate of action than that of mere agitation.

Series I.—Three quantities of cane sugar, of 10 grams each, were dissolved in about 30 c.c. of boiling water, and, after cooling, the solutions were each made up to 50 c.c. at 15·5°. All three solutions, in the 50 c.c. measures, were kept in a large vessel of cold water for two hours, and for the same time and in the same vessel of water three 50 c.c. quantities of water were kept, so as to have all at the same temperature.

Three quantities, containing 1 gram, of yeast were weighed, and to one of these, one of the 50 c.c. of water was added, and, after thoroughly mixing the yeast, the solution was added to one of the sugar solutions by pouring both, as quickly as possible, into a conical measure-glass standing in the vessel of water. Air was passed through this solution, *a*, and the temperature was 19·5°.

b. Another of the quantities of yeast was similarly treated, and a current of carbonic anhydride was passed through the solution.

c. The third quantity of yeast was treated as in *a* and *b*, and the solution was kept stirred by hand for one hour, this being the duration of the three experiments, the time being taken from the moment the solution of sugar and the water containing the yeast in suspension were mixed.

The following numbers express the velocity of the hydrolysis for all three experiments:—

	Grams of sugar inverted.	Fraction x.	K, value of $\frac{1}{\theta}\log\frac{1}{1-x}$.
Series I, *a*, *b*, and *c*...	4·864	0·4864	0·00482

The results of the series of experiments which are given in Table I were obtained after the manner of *a* experiment. The quantity of sugar required for any percentage solution was dissolved, as described, in a 50 c.c. measure, and the quantity of yeast for each experiment had added to it 50 c.c. of water. At the time mentioned in column 4 of the Table, a sample, about 12 c.c., of the solution, was poured into a small beaker containing a drop of strong potassium hydrate and a pellet of paper pulp; after thoroughly mixing the sample, it was filtered. The opticity of the filtrate was determined in a 100 mm. tube of a Soleil-Ventske-Scheibler polariscope.

As all the series of experiments were not performed at the same time, the yeast used was not the same for any two series; in fact, the number of series given means that 12 samples of yeast were employed. The results of any two series cannot therefore be compared, as yeast varies in its hydrolytic action, but the results of any one series are comparable.

Table I.—*Velocity of the Hydrolytic Action of Yeast.*

Series.	Grams of cane sugar per 100 c.c.	Grams of yeast.	Duration of contact in minutes, θ.	Grams of cane sugar inverted.	Fraction of sugar inverted, x.	K. Value of $\frac{1}{\theta}\log\frac{1}{1-x}$.
I.	5	0·5	30	0·818	0·1636	0·0025
			60	1·582	0·3164	0·0027
			120	2·741	0·5442	0·0028
		1·0	30	1·563	0·3126	0·0054
			60	2·741	0·5442	0·0058
			120	4·092	0·8186	0·0060
	10	0·5	30	1·042	0·1042	0·0016
			60	1·544	0·1544	0·0012
			120	2·780	0·2780	0·0012
		1·0	30	1·621	0·1621	0·0025
			60	2·894	0·2894	0·0024
			120	5·096	0·5096	0·0025
	20	0·5	30	1·254	0·0627	0·0009
			60	1·700	0·0850	0·0006
			120	2·934	0·1467	0·0006
		1·0	30	1·700	0·0850	0·0013
			60	2·857	0·1423	0·0012
			120	5·560	0·2780	0·0012
	30	0·5	30	1·100	0·0366	0·0005
			60	1·486	0·0495	0·0003
			120	2·586	0·0862	0·0003
		1·0	30	1·621	0·0540	0·0008
			60	2·683	0·0894	0·0007
			120	4·671	0·1556	0·0004
II.	10	0·4	60	2·104	0·2104	0·0017
			120	3·726	0·3726	0·0017
			360	8·010	0·8010	0·0019
III.	20	0·8	63	5·600	0·2800	0·0022
			120	9·160	0·4532	0·0022
			158	10·964	0·5482	0·0021

TABLE I—*continued.*

Series.	Grams of cane sugar per 100 c.c.	Grams of yeast.	Duration of contact in minutes, θ.	Grams of cane sugar inverted.	Fraction of sugar inverted, x.	K. Value of $\frac{1}{\theta} \log \frac{1}{1-x}$.
IV.	10	0·8	60	5·579	0·5579	0·0059
			120	8·090	0·8090	0·0060
	20	0·8	60	5·560	0·2780	0·0023
			120	9·460	0·4730	0·0023
V.	20	0·8	62	4·054	0·2027	0·0016
			122	6·680	0·3340	0·0015
			302	12·620	0·6310	0·0014
VI.	20	0·8	47	2·430	0·1215	0·0012
			242	10·160	0·5080	0·0012
VII.	10	0·8	60	3·918	0·3918	0·0036
			120	6·467	0·6467	0·0037
			180	7·934	0·7934	0·0037
	20	0·8	60	4·362	0·2181	0·0018
			120	7·413	0·3706	0·0017
			180	10·690	0·5345	0·0018
VIII.	5	0·8	60	2·509	0·5018	0·0050
	10	0·8	60	2·710	0·2710	0·0023
IX.	10	0·8	60	3·494	0·3494	0·0031
			120	5·880	0·5880	0·0032
	20	0·8	60	3·822	0·1911	0·0015
			120	6·180	0·3090	0·0013
X.	5	0·8	30	1·390	0·2780	0·0047
			60	2·393	0·4786	0·0047
			120	3·436	0·6872	0·0042
	10	0·8	30	1·467	0·1467	0·0023
			60	2·471	0·2471	0·0021
			120	4·324	0·4324	0·0021
	20	0·8	30	1·505	0·0752	0·0011
			60	2·277	0·1338	0·0010
			120	4·400	0·2200	0·0009
XI.	2	0·2	42	0·498	0·2490	0·0029
			80	0·826	0·4130	0·0029
			109	1·000	0·5000	0·0028
			200	1·482	0·7410	0·0029
			258	1·637	0·8185	0·0029

TABLE I—*continued.*

Series.	Grams of cane sugar per 100 c.c.	Grams of yeast.	Duration of contact in minutes, θ.	Grams of cane sugar inverted.	Fraction of sugar inverted. x.	K. Value of $\frac{1}{\theta}\log\frac{1}{1-x}$.
XI.	4	0·2	44	0·552	0·1380	0·0014
			75	0·899	0·2247	0·0015
			124	1·405	0·3510	0·0015
	6	0·2	70	0·856	0·1420	0·0009
			115	1·378	0·2296	0·0009
XII.	2	0·4	50	0·826	0·4130	0·0046
			75	1·135	0·5670	0·0048
			100	1·444	0·7220	0·0055
	6	0·4	50	1·069	0·1780	0·0017
			80	1·680	0·2800	0·0017
			115	2·362	0·3930	0·0019

It will be seen that although the value of K for any one condition of the transformation is not a constant for all the observations, as theory requires, the variation is but slight. Besides errors of observation, particularly in the low or short time factors, there is an error in not taking into account the variation in the volume of the solution due to hydration of the sugar. This, however, is not a very serious error, as the concentration which takes place in a complete hydrolysis of a 10 per cent. solution of cane sugar is only 0·2 c.c.

The errors of observation are, however, important factors when we come to consider the value of the constant. If, for example, in Table I, Series I, third experiment, there was an error of ± 0·1 division in the reading and in taking the duration of contact there was an error more or less of half a minute, there would be introduced an error of 0·0001 to 0·0002 in the value of the constant. Again, as the temperatures of all the solutions of any series may not be exactly the same, although this was aimed at when the optical observation was made, there would be an error introduced, as invert sugar varies in its opticity with the temperature. In fact, I cannot help reiterating that although the constant does not come out mathematically identical as theory requires, or as Ostwald's constant for the rate of action of sulphuric acid on cane sugar, which is as near theory as possible, yet the numbers given leave very little room for doubting that the rate of action in any series follows that of a simple chemical change.

In the course of any simple chemical change, the value of K varies with any variation in the conditions of the experiment. It will be observed in Table I to vary first with the percentage of sugar solution—the altering substance, and secondly with the amount of yeast—the active substance producing the change.

The constants obtained in the first series of experiments with 5, 10, and 20 grams of sugar, and 0·5 and 1 gram of yeast bear a very close relation to each other, and with either of the quantities of yeast they are as 4, 2, and 1; the constant is inversely as the concentration, the amount of yeast being the same; but when the proportion of yeast to sugar is the same, the constants are nearly alike. When the sugar is the same, doubling the quantity of yeast doubles the constant. If the average of the K's for the transformations brought about in the solutions of varying percentages of sugar is taken, the amount of yeast being the same, they are not quite proportionate to the percentages of sugar. Theoretically the constant should be in proportion, but inversely, as the percentage of sugar, the yeast being the same.

There are two factors which come into play which are, I think, sufficient to account for the constants not working out exactly in inverse proportion to that of the percentage of cane sugar. The first is that of the relative size of the yeast cells in solutions of cane sugar of different strengths. I find, and believe it is the first time it has been observed, that if the average size of the original yeast cell when mounted in the ale in which it has grown be taken as a standard, the average size of the cell of the same yeast when mounted in the following percentages of cane sugar is as follows:—

Original yeast	1·00
In 5 per cent. cane sugar solution	0·95
„ 10 „ „ „	0·92
„ 20 „ „ „	0·82
„ 30 „ „ „	0·77
„ 40 „ „ „	0·70

The yeast cells were measured in the solutions at the same temperature, and in a hæmatimeter where there could have been no pressure to interfere with the dimensions. In all cases the whole of the cells in one field of the microscope were drawn, and each cell measured to obtain the average number given. Indeed, anyone looking at the drawings of the cells from the sugar solutions could pick out and arrange them in the above order without having recourse to actual measurement.

The decrease in the size of the cells is no doubt due to the absorption of water from the protoplasm of the cell. This is quite in accord with what De Vries has shown for vegetable cells immersed in a solution of potassium nitrate (Sachs, *Physiology of Plants*, "Plasmolysis").

The second factor is the viscosity of the cane sugar solutions, which increases with their strengths. From careful determinations made under the same conditions and at the same time and temperature, the viscosities of the following solutions of cane sugar when compared with water were found to be—

Water				1·00
5 per cent. cane sugar solution				1·16
10	,,	,,	,,	1·33
20	,,	,,	,,	1·81
30	,,	,,	,,	2·62
40	,,	,,	,,	4·41

As, therefore, the size of the yeast cell diminishes and the viscosity of the solution increases with increase in the percentage of sugar, it might be expected that the constant for the increasing percentages of sugar would be less than inversely proportional to the strength, the amount of yeast being the same.

Influence of Breaking the Yeast Cells on the Velocity of the Hydrolytic Action.

It appeared possible that if a number of the cells of any quantity of yeast employed in an experiment were broken, and their protoplasmic contents thereby brought into solution, that the velocity of the hydrolytic action might be increased. This, however, is not so, as will be seen from the following experiments:—

Series I.—Three quantities of yeast of 0·5 gram each were taken; one of them, *a*, was pulverised in an agate mortar with about 3 c.c. of water for 45 minutes, then it was washed into a 50 c.c. measure and made up with water to that volume; the second quantity of yeast, *b*, was pulverised for the same time but without the addition of water, and made up to 50 c.c. as in *a*.

To *a*, 50 c.c. of a 10 per cent. solution of sugar were added.

To *b*, a like quantity of the sugar solution was added.

To *c*, the third quantity of yeast, unbroken, made up to 50 c.c. solution, the same quantity of the sugar solution was added.

Series II.—The experiments just mentioned were repeated with another sample of yeast. In c_1, the yeast was treated as in *c*, and b_1 as in *b*.

Series III.—2 grams of yeast were pulverised as before, without water, for one hour, and to the apparently dry powder thus obtained

25 c.c. of water were added, and the yeast was well mixed up with it.

Two quantities of sugar of 10 grams each were dissolved and made up to 50 c.c., and to one of them, a_2, 7·5 c.c. of the yeast mixture, in 50 c.c. of water, were added; and to the other, b_2, 15 c.c. of the yeast mixture, in a like quantity of water, were added.

The time of starting each experiment was taken, when the yeast mixture and sugar solutions were added, and air was passed through the solutions during the progress of the reaction.

The results of these three series of experiments are given in Table II.

TABLE II.—*The Velocity of the Hydrolytic Action of Broken compared with that of Unbroken Yeast.*

Series.	Experiment.	Grams of cane sugar per 100 c.c.	Grams of yeast.	Duration of contact in minutes, θ.	Grams of cane sugar inverted.	Fraction of sugar inverted, x.	K. Value of $\frac{1}{\theta}\log\frac{1}{1-x}$.
I.	*a*	5	0·5	60	2·549	0·509	0·00515
				120	3·900	0·780	0·00548
	b	,,	,,	60	1·737	0·347	0·00300
				120	2·548	0·509	0·00257
	c	,,	,,	60	2·549	0·509	0·00515
				120	3·900	0·780	0·00548
II.	c_1	,,	,,	60	2·934	0·587	0·00637
				120	4·208	0·841	0·00660
	b_1	,,	,,	60	1·467	0·293	0·00250
				120	2·355	0·471	0·00230
III.	a_2	10	0·6	30	1·158	0·1158	0·00178
				60	1·698	0·1698	0·00134
				180	3·861	0·3861	0·00118
	b_2	,,	1·2	30	1·583	0·1583	0·00249
				60	2·471	0·2471	0·00205
				180	5·482	0·5482	0·00191

A microscopical examination of the yeast, as used in *b*, *c*, b_1, and in Series III experiments, showed that many of the cells were crushed, and as a further proof of the protoplasm having come outside the cell sac, the filtrates obtained from these experiments, on being kept for 48 hours, showed a complete inversion of the sugar; invertase went into solution which carried on the inversion after filtration. This was not the case with the unbroken yeast.

It is seen here that when the yeast cell is broken in the presence of water, the velocity of the hydrolysis is the same as that of the unbroken yeast, and that when the yeast is broken in the dry state, and it is apparently quite dry after being pulverised for 45 minutes, the velocity is very considerably reduced. From the results given in Series III, it will be seen that the time taken to hydrolyse a given percentage of cane sugar is almost in inverse proportion to the amount of broken yeast employed, and that the constant is nearly directly proportional as in the case of unbroken yeast.

Fernback (*Ann. Inst. Pasteur*, **9**, 90) and O'Sullivan and Tompson (*loc. cit.*) found that, in working with invertase, they were unable to find any relation between the amount of invertase employed and its action, until the proper quantity of acid was added. Under the most favourable conditions of acidity, O'Sullivan and Tompson found that the hydrolytic action was in proportion to the quantity of invertase employed, or the time taken to invert any percentage of cane sugar was in inverse proportion to the quantity of invertase.

The results given in Table I show that the hydrolytic action of yeast is in proportion to its quantity without the addition of acid, and from this it is certain that the action of invertase in the healthy yeast is not the same as that of invertase prepared from it. This is the only difference between the action of yeast and that of invertase without the acid. This difference is to be accounted for by assuming, and I believe it is a correct assumption, that the invertase as it acts in the yeast has the most suitable amount of acidity in the protoplasm of the cell, and that, in the preparation of invertase, this acid, being soluble, is lost to the invertase. Invertase, no matter how it is prepared, is slightly alkaline; the extract of crushed healthy yeast is slightly acid.

I prepared invertase from yeast by allowing it to remain in contact with ether for 14 days, and then extracting the yeast with water, after evaporating the ether at 30°. This water extract precipitated with alcohol gave a copious precipitate of active invertase, which was dehydrated with alcohol (0·82), and dried over sulphuric acid in a vacuum. With the soluble portion of the invertase thus prepared, I made two series of experiments after the manner described for yeast (Mode of Procedure, p. 927), and found that although the rate of action in any percentage of cane-sugar followed closely that of yeast, yet, doubling the quantity of invertase had no material influence on the value of the constant or rate of action.

There is also a difference between the action of yeast on cane sugar and that of invertase under the most suitable conditions of acidity. If the opticity of a filtrate from a cane sugar solution, undergoing inversion by means of yeast, is taken immediately after filtration, it will be found to possess no bi-rotation; this is not the case with invertase under the most suitable conditions, as shown by O'Sullivan and Tompson (*loc. cit.*).

Influence of Ether on the Velocity of the Hydrolytic Action.

Claude Bernard in his investigation of the influence of anæsthetics on fermentation, and on the germination of seeds, showed that if yeast is placed in etherised water and cane sugar, its power of producing alcoholic fermentation is arrested, although its power of hydrolysing the sugar goes on. He also showed that the internal changes which take place in a seed during germination are not arrested by treating the seeds with ether, although the organising or building up function of the seed is arrested.

The following experiments were made in order to see if ether has any influence on the hydrolytic action of yeast.

Three quantities of yeast of 0·5 gram each were taken. To one, *a*, 2 c.c. of ether were added, and after well mixing, it was allowed to stand for 20 minutes; it was then made up to 25 c.c. with water, and added to 25 c.c. of a 20 per cent. solution of cane sugar. To *b*, the second quantity of yeast, 25 c.c. of etherised water containing 2 c.c. of the same ether as in *a* were added, and after standing for 20 minutes, it was added to 25 c.c. of the sugar solution. To *c*, the remaining quantity of yeast, 25 c.c. of water were added, and this was added to a similar quantity of the sugar solution.

Air was passed through the solutions, and the start of each experiment was taken at the time the sugar solution and the water containing the yeast in suspension were added. At the expiration of 60 minutes in each case, the solution was rapidly made up to 100 c.c., and after mixing well, about 20 c.c. were removed. One half of this was filtered, the filtrate being received in a small beaker containing a drop of potassium hydrate; the other half was simply filtered.

TABLE III.—*The Influence of Ether on the Velocity of the Hydrolytic Action.*

Experiment.	Cane sugar in grams per 100 c.c.	Grams of yeast.	Duration of contact in minutes, θ.	Grams of sugar inverted.	Fraction of sugar inverted, x.	K. Value of $\frac{1}{\theta}\log\frac{1}{1-x}$.
a	5	0·5	60	1·814	0·363	0·00326
b	,,	,,	,,	2·316	0·463	0·00475
c	,,	,,	,,	2·316	0·463	0·00475

The filtrates from *b* and *c* experiments, with and without potassium hydrate, were found to have the same opticity after 48 hours standing; this, however, was not so with the filtrate obtained from *a* without potassium hydrate; a further inversion of 1·7 grams of sugar per 100 c.c. took place in 48 hours.

Here it is seen that the action of the yeast is diminished by adding the ether directly to it, and that the cell sac is so altered as to allow the invertase to go into solution. Now, as the same amount of ether, but in a more diluted state, had no influence either on the rate of action or on the cell sac, I believe the influence of ether when added directly to the yeast is to be accounted for in the following manner, which is a most probable explanation of the retarding influence on the hydrolytic power of yeast of any neutral substance which alters the cell sac, so that the invertase leaves the cell.

When any neutral substance alters the cell sac, it also alters the protoplasm of the cell, and by so doing the soluble acid is freed from it, and goes into solution with that portion of the invertase which passes through the sac. It is easy to see how the most suitable relation of acid to invertase would under this condition be interfered with both inside and outside the yeast cell, so that in neither case is the invertase under the most favourable condition for its action.

If yeast is allowed to remain in contact with water containing 10 per cent. of ether (free from acid) for 60 minutes, the extract will be found to contain both acid and much invertase, whilst if the same quantity of yeast is similarly treated with water, the extract will be found to contain only acid.

From experiments made to determine the relative amounts of acid extracted from yeast by etherised water, and water alone, I found that the former extracted about twice as much as the latter. (See Influence of Acid, Table V.)

Influence of Potassium Hydrate on the Hydrolytic Action.

Kjeldahl (*Meddelser fra Carlsberg Laboratoriet*, 1881, **3**, 186) and O'Sullivan and Tompson (Trans., 1890, **57**, 852) show that caustic alkalis even in small quantities completely arrest the hydrolytic action of invertase. This influence of potassium hydrate is also noticeable in the case of yeast; however, if the potassium hydrate is neutralised by acid, the action is partially retrievable under certain conditions, and I find that this holds good for invertase also.

Series I.—Three quantities of sugar of 5 grams each were dissolved in 40 c.c. of water. To one, *a*, 10 c.c. of decinormal potassium hydrate were added, and to the second, *b*, there was added a like quantity of potassium hydrate. After adding the alkali to these solutions, 2 grams of yeast were added to each, and they were allowed to stand, after well mixing, for 150 minutes. *a* solution was then neutralised with 10 c.c. of decinormal sulphuric acid, and was rapidly made up to 100 c.c. *b* was made up to 100 c.c., but without the addition of acid. 2 grams of the yeast were mixed, in about 50 c.c. of water, and added to the remaining sugar solution, *c*, as rapidly as possible, and then made up to 100 c.c.

Series II.—Three quantities of yeast of 0·5 gram each were weighed, and to one, *a*, 25 c.c. of a 10 per cent. sugar solution and 5 c.c. of decinormal potassium hydrate were added; another, *b*, of the yeasts was similarly treated. These solutions were allowed to stand for 40 minutes, and then to *a* 5 c.c. of decinormal sulphuric acid were added, and to *b* 5 c.c. of water. At the time these solutions were made up to 35 c.c., there were 25 c.c. of the same sugar solution, and 10 c.c. of water added to the remaining 0·5 gram of yeast.

Series III.—Five quantities of sugar of 5 grams each were dissolved in 25 c.c. of boiling water, and the solutions, *a*, *b*, *c*, *d*, and *e*, cooled to 16°.

To *b*, 10 c.c. of decinormal potassium hydrate were added, and then 1 gram of yeast was well mixed into the solution.

c was similarly treated.

To *d*, 20 c.c. of decinormal potassium hydrate were added, and I gram of yeast was well mixed into the solution.

e. This solution was laid aside, and 1 gram of the yeast suspended in 25 c.c. of water containing 10 c.c. of decinormal potassium hydrate was kept in readiness for it.

a. This solution was laid aside.

After these solutions had stood for three hours,

b was rapidly made up to 100 c.c.

c. To this, 10 c.c. of decinormal sulphuric acid were added, and the solution was quickly made up to 100 c.c.

d. This had 20 c.c. of decinormal sulphuric acid added to it, and was then rapidly made up to 100 c.c.

e. To this solution the alkaline yeast mixture was added, and then rapidly made up to 100 c.c.

a. To this solution, 1 gram of yeast, well mixed up in 25 c.c. of water, was added, and the solution rapidly made up to 100 c.c.

Series IV.—Three quantities of yeast, of 1 gram each, were taken.

To *a*, 50 c.c. of water containing 10 c.c. of decinormal potassium hydrate were added.

b. This was treated as in *a*.

These solutions were allowed to stand for 40 minutes; then—

a had added to it 50 c.c. of a 10 per cent. cane sugar solution;

b had added to it 50 c.c. of a 10 per cent. cane sugar solution, in which there were 10 c.c. of decinormal sulphuric acid to the 50 c.c.

To *c*, the third gram of yeast, 50 c.c. of water were added, and, after well mixing, 50 c.c. of the 10 per cent. cane sugar solution.

The results of these series of experiments are given in Table IV. The start of every experiment mentioned was taken at the time the sugar solution was added to the suspended yeast, and air was passed through in all cases during the progress of the action; in fact, the results given in Table IV were obtained in the manner described under the head of Mode of Procedure.

Potassium hydrate is known to dissolve from yeast its protoplasm, and it is shown in Series III, *a*, *b*, and *c* experiments, Table IV, that if a quantity of that agent which is sufficient in the presence of sugar to almost completely retard the hydrolytic action of yeast is neutralised with acid, the change goes on nearly at the same rate as with the original yeast. Now the questions suggest themselves, Does potassium hydrate dissolve invertase from the yeast? and, Has the yeast afterwards a greater or less hydrolytic action than that of its

TABLE IV.—*The Influence of Potassium Hydrate on the Velocity of the Hydrolytic Action.*

Series.	Experiments.	Cane sugar in grams per 100 c.c.	Grams of yeast.	Duration of contact in minutes, θ.	Grams of sugar inverted.	Fraction of sugar inverted, x.	K. Value of $\frac{1}{\theta}\log\frac{1}{1-x}$.
I.	*a*	5	2	30	1·154	0·230	0·00379
	b	,,	,,	50	none	none	0
	c	,,	,,	50	4·092	0·818	0·01479
II.	*a*	7·14	1·42	60	4·208	0·589	0·00643
	b	,,	,,	60	none	none	0
	c	,,	,,	60	5·405	0·757	0·01024
III.	*a*	5	1	60	3·745	0·749	0·01000
				120	4·520	0·904	0·00900
	b	,,	,,	60	0·465	0·092	0·00070
				120	0·656	0·131	0·00050
	c	,,	,,	60	3·281	0·656	0·00772
				120	4·324	0·865	0·00724
	d	,,	,,	60	0·465	0·092	0·00070
				120	0·656	0·131	0·00050
	e	,,	,,	60	none	none	0
				120	,,	,,	0
IV.	*a*	5	1	60	,,	,,	0
	b	,,	,,	60	0·424	0·085	0·0006
	c	,,	,,	60	3·900	0·780	0·0110
V.	*a*	12·10	0·605	60	0·617	0·051	0·00038
	b	,,	,,	60	2·779	0·228	0·00187
		,,	,,	60	0·309	0·026	0·00019

potassium hydrate extract? An answer to these questions might throw some light on the state of the invertase within the yeast.

The following experiments were made with the object of arriving at information on the points just mentioned:—

Series V.—Table IV. 20 grams of sugar were dissolved in about 60 c.c. of water, 15 c.c. of decinormal potassium hydrate were added, and the solution made up to 150 c.c. To this solution, in a beaker, 1 gram of yeast was added, and, after well mixing, it was allowed to stand for three hours. At the expiration of that time, the solution was well mixed, and about 40 c.c. of it were filtered.

a. To 25 c.c. of the alkaline filtrate, free from yeast, 2·5 c.c. of decinormal sulphuric acid were added.

b. To 50 c.c. of the solution, with the yeast in suspension, 5 c.c. of acid were added.

c. To another 50 c.c. there were added 5 c.c. of water.

At the start of these experiments, all three are alike as regards sugar and yeast, and the results calculated per 100 c.c. are, therefore, comparable.

The influence of potassium hydrate is seen, from the results given in Table IV, to be more than that of simply neutralising the acidity of the yeast cell, for, in Series III, *d* experiment, the 20 c.c. of decinormal potassium hydrate, although afterwards neutralised with acid, affects the action as much as the alkalinity of 10 c.c. of potassium hydrate. The influence of this agent is no doubt a question of quantity, for strong potassium hydrate, as shown by O'Sullivan and Tompson, completely arrests the action of both invertase and yeast at 54°. The action is doubtless one of killing, or, as I would prefer to say, it is due to a breaking up of the invertase molecule.

The results of Series III and V show that if potassium hydrate is added to yeast in the presence of cane sugar, its retarding influence is not so marked as in the absence of sugar, which I find is also the case with invertase. This is a curious fact, particularly when we consider that O'Sullivan and Tompson (Trans., 1890, **57**, 900) proved that invertase in the presence of cane sugar solution resists a temperature fully 25° higher than in the absence of sugar.

In Series V, it will be seen that the yeast which, in the presence of sugar, had been treated with potassium hydrate which was afterwards neutralised with acid, possesses far and away a greater hydrolytic action than the extract of the same quantity of yeast with the same proportion of potassium hydrate when similarly neutralised.

The Influence of Acid on the Velocity of the Hydrolytic Action.

Under the heading, "Influence of Ether," I explained that the effect of that substance in retarding the action was due to a variation brought about by it in the acidity of the invertase, both inside and outside the yeast cell. This explanation receives support from the following series of experiments, Table V. The experiments were carried out under identical conditions, and, as acid, I employed decinormal sulphuric acid (1 c.c. = 0·008 SO_3).

TABLE V.—*The Influence of Acid on the Velocity of the Hydrolytic Action.*

Experiment.	Grams of cane sugar per 100 c.c.	Grams of yeast.	C.c. of decinormal sulphuric acid per 100 c.c.	Duration of contact in minutes, θ.	Grams of cane sugar inverted.	Fraction of cane sugar inverted, x.	K. Value of $\frac{1}{\theta}\log\frac{1}{1-x}$.
A	10	1	0	122	7·06	0·706	0·0043
				180	8·45	0·845	0·0044
B	,,	,,	0·2	122	6·83	0·683	0·0040
				180	8·18	0·818	0·0041
C	,,	,,	0·4	122	6·64	0·664	0·0038
				180	8·11	0·811	0·0040

Here, even with the very slight quantity of acid employed, it is seen that there is a distinct retarding influence on the action, and that this is more marked in the case of the larger quantity of acid.

The filtrates obtained from B and C experiments at both periods of contact, and without the addition of potassium hydrate, were found to indicate the presence of invertase when observed 24 hours after filtration; the filtrates from A, under like conditions, were observed to indicate the absence of invertase.

Influence of the Hydrolytic Action of Yeast on its Alcoholic Fermentation Power.

In order to arrive at an answer to this question, I took four flasks of equal capacity (175 c.c.) and added to each 100 c.c. of malt wort (sp. gr. 1060). The malt wort in the flasks was boiled for half an hour, and then cooled to 20°.

a. To one, I added 25 c.c. of a filtrate from *a* experiment (Series I, Mode of Procedure, p. 927) and 0·25 gram of the same yeast as was used to bring about the hydrolytic action.

b. To another, I added 25 c.c. of *a* solution without filtering out the yeast.

c. To the third, I added 25 c.c. of a filtrate from *b* experiment (Series I, Mode of Procedure, p. 927) and 0·25 gram of the same yeast.

d. To the remaining flask, I added 25 c.c. of *b* solution without filtering out the yeast.

The flasks were provided with wash-bottles containing water to catch any alcohol which might pass over with the gas evolved during fermentation, and were laid aside under similar conditions.

As I have already shown (Part I) that yeast does not increase during its hydrolysing action, it will be seen that in taking 25 c.c. of either of the solutions *a* and *b* with the yeast in suspension, at the one hour's period of digestion, there is one-fourth of the yeast added, or 0·25 gram of yeast. The composition of the two 25 c.c. of the filtrates and the two 25 c.c. of solutions containing the yeast in suspension being the same, the four 125 c.c. quantities of solution put to ferment were the same in every way.

When the fermentation had gone on in each case for 43 hours, each solution, including the wash-water, was made up to 200 c.c. The alcohol produced in each was determined in 100 c.c., and the number of yeast cells per volume of 1/4000 cub. mm. was counted in the remaining portion of the solutions.

I is the grams of solid matter fermented out of the 125 c.c. of solutions deduced from the alcohol formed; II the number of cells per volume in the solutions:—

	I.	II.
a	8·34 grams.	11·9 cells.
b	8·25 ,,	15·7 ,,
c	8·50 ,,	13·0 ,,
d	8·20 ,,	11·9 ,,

The alcohol produced in these solutions is practically the same, and the only difference observed is the greater quantity of yeast in *b*, where the yeast, prior to being added to the solution for fermentation, had been aërated.

It is possible that in fermentation experiments, particularly where cane sugar enters largely into the composition of the sugars used, it may be desirable to determine the hydrolytic power of the yeasts employed. From Table I (p. 928, *et seq.*), it will be seen that for any one quantity of healthy yeast in any one percentage of cane sugar up to 20 per cent., if the temperature of the decomposition is the same and the solution kept agitated, the K or constant obtained at any stage in the inversion can be taken as an expression of the velocity of the hydrolytic power.

As an example of what I mean, at Series III and IV, Table I it will be seen that the constants obtained are practically the same, although the yeasts are not the same; therefore these yeasts have the same hydrolytic power; in Series VI, under like conditions, the constant is only about half what it is in III and IV, which means that the yeast in Series VI has only half the power of that used in III and IV.

If the percentage of sugar and yeast, the temperature, and the duration of contact is the same in all experiments made to determine the relative hydrolytic power of yeasts, the quantity of cane sugar inverted could, of course, be taken as a measure of the action of the yeasts employed, but there is an advantage in taking the constant as the measure, for then the time of contact need not necessarily be the same in all cases.

In conclusion, I desire to point out that Sheridan Lea has shown in a paper entitled "Some Notes on the Isolation of a Soluble Urea Ferment from the *Torula ureæ*" (*Jour. of Phys.*, **4**, 3), that although the soluble "ferment" contained in *Torula ureæ*, to which the hydrolysis of urea in urine is due, can be isolated from that organism, yet the action is not due to the secretion of the soluble "ferment" by the torula; the "ferment," in fact, does not pass out of the cells during the progress of the change. I had not seen this paper previous to the publication of Part I. Sheridan Lea mentions an experiment made with yeast and cane sugar, the result of which led him also to infer that invertase does not pass out of the yeast cell when the latter inverts cane sugar.

A portion of a solution of cane sugar which was fermented with fresh active yeast was freed from the yeast by filtration, and the filtrate added to a solution of cane sugar. This solution was observed to be "dextrorotatory," and remained so after digestion for 24 hours at 38°. I take it that Dr. Lea means the dextrorotatory power of the solution remained constant after digestion for the time mentioned.

A summary of the conclusions which I would draw from the results herein described is given.

1. The hydrolytic action of yeast at ordinary temperatures (12° to 20°) follows the same course as that of a simple chemical change, and is not influenced either by air or by carbon dioxide.

2. A time curve representing the action would correspond with that given by O'Sullivan and Tompson (Trans., 1890, **57**, 878) for invertase, under the most suitable conditions of acidity. The rate, therefore, differs from that at which the alcoholic fermentation of yeast takes place, which would be represented by a straight line (Dumas, *Ann. Chim. Phys.* [3], 1874, 81; and A. J. Brown, this vol., p. 384).

3. Any change, either by increasing or diminishing the natural acidity of the yeast cell diminishes its action. This is a very important matter, and should always be considered when dealing with organisms, or cellular membranes, possessing the power of hydrolysing cane sugar. Dumas observed that both acids and alkalis interfered with alcoholic fermentation, and that in the case of alkalis the yeast possessed the power of overcoming the alkalinity, the liquid again becoming acid and fermentation recommencing. It is found that a quantity of potassium hydrate which completely arrested the hydrolytic action of yeast for three to six hours was neutralised by the yeast in about 24 hours, the solutions eventually becoming acid and hydrolysis recommencing.

4. It is inferred, from the experiments on the effect of rupturing the cell, on the velocity of the hydrolytic action, and also from the rate at which the change proceeds, that the *whole* of the invertase of the yeast cell comes into action as soon as the cane sugar is added to the yeast, and that it continues to act during the progress of the hydrolytic action.

5. The power which yeast possesses of producing alcoholic fermentation is not altered in any way by the yeast having first hydrolysed cane sugar, and this is the case whether the hydrolytic action is brought about in the first instance in the presence of air or carbon dioxide.

LXXXII.—*Imidosulphonates.*

By Edward Divers, M.D., F.R.S., and Tamemasa Haga, F.C.S.

This paper gives the results of an investigation of the hitherto unknown sodium imidosulphonates and their derivatives, as well as of some new ammonium and potassium salts. In addition, several mixed tribasic salts which show peculiarities in their constitution are described, particularly those of lead, of silver, and of mercury. A description is also given of the experimental determination of the nature of Rose's "sulphatammon," a compound of 1 mol. of sulphur trioxide with 2 mols. of ammonia.

History.—Rose (1834—1840; *Ann. Phys. Chem.*, **32**, 81; **47**, 471; **49**, 183); Jacquelain (1843; *Ann. Chim. Phys.* [3], **8**, 293); Fremy (1845; *ibid.* [3], **15**, 408); Woronin (1859; *J. Russ. Chem. Soc.*, **3**, 273); Claus and Koch (1869; *Annalen*, **152**, 336); Berglund (1875;

L. univ. Arsk., **12** and **13**; *Bull. Soc. Chim.*, **25**, 455; **29**, 422; *Ber.*, **9**, 252 and 1896); Raschig (1887; *Annalen*, **241**, 161); and Mente (1888; *ibid.*, **248**, 232) are the chemists who have examined the inorganic salts now known as imidosulphonates.* The constitution of these salts has been established mainly through investigations by Rose, Jacquelin, and Berglund.

In 1834, Rose discovered that when the compounds of sulphur trioxide with ammonia, which he called "sulphatammon" and "parasulphatammon," are freshly dissolved in water, they give the reactions of a sulphate very incompletely or not at all, and do not yield up all their nitrogen as ammonia to chloroplatinic acid and other reagents.

Jacquelain discovered that the stable compound of sulphur trioxide and ammonia, his "sulphamide," is derived from, 2 mols. of the oxide and 3 mols. of ammonia.

Berglund determined the constitution of this stable compound to be imidosulphonic, by ascertaining that it behaves as an ordinary ammonium salt only to the extent of two-thirds of its nitrogen.

To Fremy is due the discovery that hydrolysis of the main product of the action of a nitrite upon a sulphite yields a salt, his "sulphamidate," now known to be an imidosulphonate; and that this salt exhibits the reactions which are neither those of a nitrite nor of a sulphite, and that it can be so far hydrolysed as to yield ammonia.

Fremy and, subsequently, Claus and Koch attributed to this salt a composition which was that of an addition compound of ammonia, but Berglund showed that this was incorrect, as he established the identity of Fremy's potassium sulphamidate, and Claus's "disulphammonate," with potassium imidosulphonate prepared from ammonium imidosulphonate obtained by the action of ammonia on chlorosulphonic acid. Mendeléeff (abstr. in *Ber.*, **3**, 872) had just before this suggested such a constitution as possibly belonging to Fremy's sulphamidates. In his *Principles of Chemistry* (1891), however, apparently unaware of Berglund's results, he treats parasulphatammon as being ammonium amidosulphonate. More recently, Raschig showed that the properties of Fremy's salts are inconsistent with Claus's view that they are compounds containing quinquevalent nitrogen.

Claus recognised the sulphonic constitution of these salts, whilst Berglund's discovery that they are formed by the mutual action both of sulphur trioxide and ammonia, and of sulphur dioxide and a nitrite, supplied an admirable confirmation of Claus's theory.

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* Woronin's paper we only know from abstracts in the *Jahresbericht* and *Watts' Dictionary*. Berglund's memoir also, in the *Lunds universitäts Arskrift*, we have not seen.

Although, as we shall demonstrate, Rose, Jacquelain, Fremy, and Woronin had all prepared imidosulphonates with three equivalents of base, as well as those with two, to one of nitrogen, yet no clear conception of these compounds as salts of an acid higher than bibasic had been formed before they were examined by Berglund, who showed that they were derivatives of a tribasic acid, in which both the aminic, and the sulphonic, hydrogen is basic. He was the first to prepare the tripotassium and some other analogous salts.

It will be seen that the existence of imidosulphonates with three equivalents of base, first observed by Berglund, makes the term *imidosulphonate*, which he himself introduced, a misnomer, since in these salts all the hydrogen atoms in ammonia are displaced. As, however, no simple way out of this difficulty presents itself, we have adopted the name as Raschig and Mente had done previously.

Imidosulphonic Acid.

Imidosulphonic acid, $HN(SO_3H)_2$, first prepared by Jacquelain, has only been obtained in solution. We have employed his process, which consists in treating the lead salt, suspended in water, with hydrogen sulphide, using special care to have the lead salt as free as possible from sodium. It was decomposed by the hydrogen sulphide with very sensible elevation of temperature, and this strengthened our expectation that the acid must be hydrolysed almost as fast as it is formed; this, however, was found not to be the case, as, on filtering rapidly with the aid of a vacuum pump, it gave a concentrated solution containing very little sulphuric acid, and therefore very little amidosulphonic acid.

The imidosulphonic acid was fully identified by the abundant precipitate which it gave with excess of baryta-water being readily soluble in nitric acid, with the exception of a little sulphate; and particularly by its yielding an abundant crystalline precipitate with potassium acetate. Jacquelain converted his acid into the very soluble dibarium salt by just neutralising the acid with baryta, although he was aware that excess of baryta would give him the insoluble salt. On leaving the solution of the acid in a vacuum desiccator, we found that it became almost wholly hydrolysed to amidosulphonic acid in 18 hours or less.

Fremy attempted to prepare the acid by adding hydrofluosilicic acid to potassium imidosulphonate, but found that the acid decomposed almost immediately, the products of decomposition being sulphuric acid, sulphurous acid, and ammonia, but in this he must have erred. Berglund prepared the acid as Jacquelain had done, and found it very unstable.

We find that dry dipotassium imidosulphonate may be mixed with dry potassium hydrogen sulphate, and fused without being affected. At temperatures high enough, however, 420—450°, the imidosulphonate suffers the same decomposition as when heated alone. To prevent decomposition of the salts, moisture must be excluded, and we have therefore worked in a Sprengel-pump vacuum. When the fused mixture of the two salts is cooled, powdered, and treated with alcohol or ether, only a very little sulphuric acid passes into solution.

Dipotassium imidosulphonate, in dry, fine powder, mixed with 2 mols. of sulphuric acid of sp. gr. 1·84, forms a thin paste, which, if kept in a dry atmosphere, soon solidifies to a hard, somewhat translucent mass. This when powdered and exposed to air does not deliquesce, neither does it undergo any apparent change if left for days in dry air. On dissolving such a preparation in water to which a little potassium hydroxide has been added to guard against hydrolysis, it yields much unchanged imidosulphonate, together with amidosulphonate, but no ammonia. The presence of amidosulphonate is no doubt due to water taken up from the air during mixing, and from the sulphuric acid itself, and lastly, to some degree, during its dissolution in water, in spite of the alkali present. When heated, the mass very readily fuses and gives off sulphuric acid and sulphur dioxide. Jacquelain observed a similar behaviour with sulphuric acid, hot and cold, in diammonium imidosulphonate.

The comparatively slight action of concentrated sulphuric and nitric acids was noticed by Fremy, and by Claus and Koch. No evidence, therefore, has been obtained of any action of sulphuric acid on a dry imidosulphonate such as would be expressed by the equation

$$HN(SO_3K)_2 + 2SO_4H_2 = HN(SO_3H)_2 + 2HKSO_4.$$

Ammonium Imidosulphonates.

Diammonium Imidosulphonate, $HN(SO_3NH_4)_2$.—The diammonium salt can be prepared from ammonia and sulphur trioxide (Rose, Jacquelain, Woronin), or chlorosulphonic acid (Berglund, Mente), or sulphuryl chloride or pyrosulphuryl chloride (Mente). It is obtained when nitrous gas is passed into an ice-cold solution of ammonium sulphite, and the product hydrolysed (Fremy). It is also formed together with ammonia on heating ammonium amidosulphonate to 160° (Berglund).

The decomposition of barium imidosulphonate by a solution of ammonium sulphate can only be very imperfectly accomplished, but by treating it first with dilute sulphuric acid in quantity barely sufficient to convert it into the soluble barium hydrogen salt (p. 965), and then adding ammonium sulphate until the barium is completely precipitated, diammonium imidosulphonate can be prepared in a satisfactory manner. Another method is to decompose either of the hydroxy-lead imidosulphonates (p. 970, *et seq.*) with a solution of ammonium carbonate.

Triargentic imidosulphonate (p. 974), stirred with a solution containing the equivalent quantity of ammonium bromide, has been our source of the diammonium salt. The solution of triammonium salt thus produced is decanted from the silver bromide, evaporated on a water-bath until ammonia almost ceases to be given off, and filtered from a little silver bromide. To obtain the salt in a crystalline state, the solution generally requires further evaporation, but is kept alkaline by occasionally adding a drop of strong ammonia, so as to avoid hydrolysis into amidosulphonate during the operation.

Diammonium imidosulphonate forms monosymmetric prisms, isomorphous with the potassium salt (Münzing and Raschig). In its general reactions it is like the sodium and potassium salts. It reddens blue litmus even while still quite free from sulphuric acid (Jacquelain).

The effect of heating it was tried by Rose, and is described in the first of his papers on the "sulphatammons." According to him the products differ little from those obtained on heating ammonium sulphate, except that there is no water present. Ammonia and sulphur dioxide are evolved, first the former, then principally the latter. The residue consists of acid ammonium sulphate if the temperature is not too high. In the neck of the retort, ammonium sulphite and sulphate are found; in the receiver, the former salt only. He found that, when the salt is heated in gaseous ammonia, but little sulphate is formed.

This account given by Rose of the effect of heating diammonium imidosulphonate is essentially incomplete, but is true to the extent that ammonia, first, and then sulphur dioxide, are evolved, that these two partly condense as a sublimate, and that acid sulphate is formed. Heating in a roomy retort, and thus permitting the action of moist air, favours the change here described, and brings it still nearer to that caused by the action of heat on ammonium sulphate.

Jacquelain states that it is fusible without decomposition, and may be kept fused without change if heated in a current of dry ammonia, but that, a little above its melting point, it decomposes into ammonia, and ammonium sulphite, which sublimes, whilst a residue of ammonium hydrogen sulphate is left.

We are unable to confirm this. Diammonium imidosulphonate, which heated in a vacuum, suffers no change (except that it yields a very minute liquid sublimate at 190°) until very near to 357°, when it melts and effervesces or boils. Most of the vapours condense as unchanged imodosulphonate just above the heated part of the tube, but a little ammonia is given off. At last, inconsiderable sublimates, white and yellow, appear some distance up the tube, consisting of compounds of ammonia with sulphur dioxide, and during their formation, minute quantities of nitrogen are liberated. On stopping the operation in an hour or two, when the evolution of gas is scarcely noticeable, the residue is found to be unchanged imidosulphonate mixed with a little acid sulphate. When the salt is subjected to a stronger heat, so as to be kept in violent ebullition, most of the unchanged salt condenses and flows back, and but little of it is got as a sublimate. On the other hand, there is more of the sulphite-ammonia sublimates, although they are still not abundant, and nitrogen is now given off more freely; the quantity, however, as well as that of the ammonia, is small, even if the heating is maintained for a long time. In one experiment, after about an hour's violent ebullition, the residue on being dissolved in sodium hydroxide solution in a closed vessel, and titrated with acid, was found to contain about one-fifth of its weight of ammonium pyrosulphate.

From what precedes it is evident that diammonium imidosulphonate is a comparatively stable compound, boiling and for the most part condensing unchanged. It, however, decomposes, but only very slowly, even when more strongly heated, into nitrogen ammonia, water, sulphur dioxide, and sulphur trioxide, thus:—

$$6HN(SO_3NH_4)_2 = 2N_2 + 14NH_3 + 6H_2O + 6SO_2 + 6SO_3,$$

these products then partly condensing, and yielding, finally,

$$2N_2 + 2NH_3 + 3S_2O_5(NH_4)_2 + 3O(SO_3NH_4)_2.$$

The ammonia first given off unmixed with nitrogen is no doubt attributable to the action of moisture in the somewhat deliquescent salt. This water would cause the hydrolysis of its molecular equivalent of the salt into amidosulphonate and acid sulphate, and then, by further heating, into pyrosulphate and ammonia:—

$$HN(SO_3NH_4)_2 + H_2O = H_2N\cdot SO_3NH_4 + HO\cdot SO_3NH_4 = H_3N + O(SO_3NH_4)_2.$$

Experiments by one of us, as yet unpublished, have fully established the existence of the undescribed salt, ammonium pyrosulphate, $O(SO_3NH_4)_2$, referred to above.

Triammonium Imidosulphonate (hydrated).—This salt, hitherto undescribed, is formed by the union of ammonia with diammonium imidosulphonate in presence of water. The ammonia must be in excess, otherwise the salt is partly decomposed by water. The most concentrated ammonia solution precipitates it from a saturated solution of the diammonium salt; also from a concentrated solution of the disodium salt, but in that case it is mixed with sodium ammonium salt (p. 961). Gaseous ammonia acts similarly and much more effectively. As thus obtained, it is a crystalline powder, but it can be got in large crystals by dissolving it, or the diammonium salt, to saturation in moderately strong ammonia, in a closed vessel by the aid of heat, and allowing the solution to cool. The largest crystals are prepared by evaporating its ammoniacal solution in a desiccator, over solid potassium hydroxide, and in a strongly ammoniacal atmosphere.

The crystals resemble those of the tripotassium salt, and are, therefore, asymmetric. They are clear and lustrous, but gradually effloresce (mostly through loss of ammonia), and become opaque and damp. The salt when dry smells faintly of ammonia, and its crystals in a dry ammoniacal atmosphere over solid potassium hydroxide very slowly become anhydrous and opaque throughout, while retaining much of their lustre and hardness.

When heated, the salt is converted mainly into the diammonium salt, but to some extent it melts, loses both ammonia and water, and hydrolyses into sulphate.

If dissolved in water, it decomposes, but very incompletely, into the diammonium salt and ammonia, and the solution when evaporated in the open air yields crystals of the diammonium salt only. Hence, when either the trisodium or the tripotassium salt is mixed with ammonium chloride, much ammonia is liberated.

It was analysed sufficiently by heating it to 160° very gradually in a current of dried air, in order to determine the water and third atom of ammonia. The sulphur was also estimated, and the salt was thus proved to have a composition analogous to that of the potassium salt, namely, $NH_4{\cdot}N(SO_3NH_4)_2,OH_2$. The crystals, after rapid pressure in filter paper, were damp but transparent, and when analysed gave the following results:—

	Calculated.	Found.
Sulphur	26·0	25·4
Loss at 160°	14·2	16·0

Anhydrous Triammonium Imidosulphonate; "*Sulphatammon.*"—Anhydrous triammonium imidosulphonate is, as we shall show, Rose's sulphatammon. Rose found that dry ammonia conducted into a flask lined with sulphur trioxide combines with the trioxide yielding two products, one a hard, vitreous matter, replacing the lining of sulphur trioxide, the other a loose, flocculent deposit.

Jacquelain got the same flocculent substance when he mixed vapour of sulphur trioxide with dry ammonia in excess. Rose found that both the flocculent and vitreous matters when dissolved in water and evaporated yielded crystals of the same substance, but that the vitreous matter was often acid, through, as he considered, imperfect action of the ammonia. The crystals which he separated from the solution he called *parasulphatammon;* they are now known to be diammonium imidosulphonate, and from what we ourselves have seen of sublimed diammonium imidosulphonate, we have very little doubt but that the vitreous matter is the same salt, and that the acid reaction occasionally observed is due to hydrolysis. From this it follows that the crystals are formed from three volumes of ammonia and two of sulphur trioxide, whilst Rose made out that they had the same composition as the undissolved flocculent matter, and were formed therefore from two volumes of ammonia and one of sulphur trioxide. He recognised, however, such differences in their properties that he held them to be distinct, and called the flocculent matter *sulphatammon.* Jacquelain prepared parasulphatammon from the flocculent matter by two methods, both without the use of water. He found it to be variable in composition, and one of his methods of getting crystalline pure parasulphatammon from it was to fuse it in a current of ammonia, allow it to solidify, and then stop the further entrance of ammonia before it cooled. His other method was to expose the flocculent matter, first, over sulphuric acid in a vacuum till it ceased to lose weight, and then to a moderate heat, which caused a further loss.

Having in a most careful manner proved that Rose's analysis of parasulphatammon was incorrect, Jacquelain himself no less strangely misconstrued the facts he had correctly observed. He found that parasulphatammon, prepared by the action of heat, if allowed to cool in contact with ammonia, absorbed it; further that the flocculent matter, named sulphatammon by Rose, would lose from 6 to 9 per cent. of its weight in a vacuum over sulphuric acid, and the residue, if heated to 100°, gave up more ammonia, leaving parasulphatammon, as already mentioned. But he treated these phenomena as a case of the physical absorption of gases by porous solids, and likened the ammonia lost or taken up to hygroscopic moisture. Yet a compound of 2 mols. of sulphur trioxide with 4 mols. of ammonia has to lose as ammonia only $7\frac{1}{2}$ per cent. of its weight in order to become a compound of 2 mols. of sulphur trioxide with 3 of ammonia. As for the high loss of 9 per cent. recorded, that, if correctly observed, may have been due to loss of moisture, for, as Rose found, sulphatammon is markedly hygroscopic, and loses the moisture again at 100°.

Sixteen years later, Woronin first established the accuracy of Rose's analysis of the flocculent matter, sulphatammon, and then showed that this and parasulphatammon were different salts of the same acid. Another 16 years later, Berglund claimed for sulphatammon that it must be triammonium imidosulphonate, since parasulphatammon had proved to be diammonium imidosulphonate. But then, opposed to this conception of its nature there were the facts, first, that Rose had made no mention of its evolving ammonia when it was dissolved in water, and evaporated, so as to yield parasulphatammon; secondly, that Raschig, much more recently, had dissolved an old specimen of parasulphatammon in ammonia solution, and on evaporation over sulphuric acid got only parasulphatammon again; and, lastly, what is known to ourselves, at least, that trisodium, or tripotassium, or triargentic imidosulphonate, when decomposed by ammonium chloride solution, sets free much ammonia. It seemed to us, therefore, at first to be as evident as it was probable that imidosulphonic acid could not fix a third atom of ammonia along with its imidic hydrogen, and that Berglund's view might not be right.

Experiment has, however, established that sulphatammon is, as Berglund considered it, the triammonium salt. Crystals of the diammonium salt were coarsely ground (they are somewhat hygroscopic, as just stated, and slip under the pestle, and so are not readily ground fine), and of this powder, a quantity equal to 2·29 grams if dried at 100°, was exposed to a current of carefully dried ammonia, of which it absorbed in two hours 5¾ per cent., and in two hours more another ½ per cent., making altogether 6¼ per cent., the temperature being 20°; the calculated quantity is 8 per cent., but, considering the coarseness of the particles and the temperature, the result obtained may be regarded as satisfactory. The absorption of ammonia was attended with a very considerable change in the volume of the solid, and converted it into a bulky non-coherent, amorphous powder, the odour of which was only feebly ammoniacal. When dissolved in water, it became strongly ammoniacal, and the solution gave a copious precipitate with barium chloride, and otherwise behaved as a solution of the crystalline hydrated salt, which salt, indeed, it yielded when treated with gaseous ammonia. Evaporation of the solution gave crystals of the diammonium salt, which is just what Woronin observed with sulphatammon, the latter being converted into parasulphatammon.

On exposing it in a desiccator over sulphuric acid for three days at a temperature of about 20°, we found that it lost only about ½ per cent. of its weight, so that probably the pure dry salt loses ammonia only in a damp atmosphere, although indeed Jacquelain has found sulphatammon (probably damp) sometimes give up much ammonia in a vacuum over sulphuric acid. Having observed the loss of ammonia to be so slight at the ordinary temperature, we heated the same portion in a current of well-dried air for 1¾ hours at a temperature of 100—120°, and then found that the issuing air still contained ammonia. The salt cooled and reweighed had lost only 5·4 per cent. in weight during this heating, and when dissolved in water and tested showed that some triammonium salt was still present.

From what precedes, it is evident that triammonium imidosulphonate is comparatively stable in the anhydrous state, and that Rose's sulphatammon is this salt. Formed, as here described, from another imidosulphonate without hydrolysis, it cannot be ammonium amidosulphonate, as it is commonly assumed to be (as in Mendeléeff's *Principles of Chemistry* and Ramsay's *System of Inorganic Chemistry*). Further, its conversion by heat into parasulphatammon and ammonia affords no proof that it is ammonium amidosulphonate, for the latter would only be changed at temperatures above 160°. A salt which is certainly ammonium amidosulphonate can be prepared by processes which include the hydrolysis of an imidosulphonate, but it is quite a different substance. According to Berglund, it crystallises in large plates, and is not converted into imidosulphonate and ammonia unless it is heated at 160°. It is not readily decomposed by water, is neutral in reaction, and does not precipitate barium salts, facts verified for us by Mr. Y. Osaka.

Imidosulphonamide, $HN(SO_2{\cdot}NH_2)_2$.—Mente finds that this compound is produced by the action of ammonia upon pyrosulphuryl chloride. Diammonium imidosulphonate, when heated to its subliming point, may possibly yield it, but as at ordinary temperatures it reacts at once with water to form diammonium imidosulphonate, its presence cannot be tested for.

Potassium Imidosulphonates.

Dipotassium Imidosulphonate.—This salt was obtained by Fremy by the hydrolysis of potassium nitrilosulphonate, formed by the action of sulphite upon nitrite. Claus and Raschig have both published accounts of the preparation of the salt in this way. It has also been obtained by double decomposition from diammonium imidosulphonate and a potassium salt (Fremy, Berglund); also by Woronin from the diammonium salt by converting it into Jacquelain's barium salt and decomposing that with potassium sulphate.

Imidosulphonates may be readily enough prepared from nitrilosulphonates by hydrolysis, but as the two potassium salts are only sparingly soluble in water, and the imide salt very readily passes into the amide salt by further hydrolysis, the method of preparation of dipotassium imidosulphonate hitherto employed gives very uncertain results. On the other hand, the conversion of sodium nitrilosulphonate into disodium imidosulphonate can be effected very easily and completely; and as the disodium imidosulphonate is very soluble, the insoluble potassium salt can be prepared from it by double decomposition without any trouble. Prepared in this way, it is very pure, and consequently stable. It can also be recovered from mercuric dipotassium imidosulphonate by the action of nitric acid (p. 977).

Dipotassium imidosulphonate is also formed when potassium amidosulphonate is heated. Our earliest knowledge of this interesting change—$2H_2NSO_3K = H_3N + HN(SO_3K)_2$—is due to Berglund. We ourselves find that at or just below 350° this change takes place readily, the gas evolved being ammonia, and free from nitrogen. At this temperature, the salt fused, and then gradually solidified as the decomposition proceeded; the salt we used was not pure, however, being mixed with potassium sulphate.

The effect of heat on dipotassium imidosulphonate has also been studied by us. Below the softening point of soft lime-glass, the dry dipotassium salt in a dry atmosphere does not undergo any notable change, but in a Sprengel vacuum, it evolves gas, although very slowly and of very low tension, and yields a very slight sublimate between 360° and 440°. At the temperature of actual decomposition, it melts and boils, the change which occurs being expressed by the equation

$$3HN(SO_3K)_2 = N_2 + NH_3 + 3SO_2 + 3K_2SO_4.$$

The ammonia and some of the sulphur dioxide unite to form a rather volatile, yellowish-brown sublimate, and a less volatile, white sublimate, both of which readily give the reactions for ammonia and sulphur dioxide when dissolved in water. The brown sublimate gives a clear, colourless solution. Both sublimates appear to have been obtained by Rose from sulphur dioxide and ammonia. Probably, judging from Mente's researches, the yellow compound is nitrogen sulphide, and the white is sulphamide. The permanent gases consist of one volume of nitrogen to somewhat more than two of sulphur dioxide. We had expected to be able to get evidence of the intermediate formation of nitrilosulphonate—$3HN(SO_3K)_2 = H_3N + 2N(SO_3K)_3$—by arresting the decomposition before it had gone very far, and by carefully regulating the temperature, but we were as unsuccessful as in the case of the diammonium salt.

Fremy observed that the action of heat gave rise to potassium sulphate, sulphur dioxide, ammonia, and a coloured sublimate. Claus and Koch recorded the decomposition of the salt above 200° sharply with the same results. But neither chemist mentions the still more abundant white sublimate, and, what is of more significance, the nitrogen; had they done so, it would have been seen that the salt is not an addition compound of ammonia, as they supposed.

One of the remarkable properties possessed by imidosulphonates, as well as by oximidosulphonates, is that of hydrolysing at a sufficiently high temperature by fixing the moisture of the air. Claus had observed slow increase in weight of potassium nitrilosulphonate and of oximidosulphonate (his trisulphammonate and disulphydroxyazate) when they were heated in the air, but wrongly ascribed this increase to oxidation. Oxidation it could not be, for this would only give rise to volatile products, such as water, or oxide of nitrogen, or nitrogen itself, and not increase the weight of the fixed matter. We have, besides, fully proved by experiment that at the temperature at which any imidosulphonate increases in weight in ordinary air, or even at a higher one, that salt remains for hours unchanged in weight and appearance if the air is dried, and yet if the air is undried it begins to increase in weight. The product of hydrolysis produced by the moisture in ordinary air causes the imidosulphonate to lose its crystalline lustre, cake together, and become acid. In order to prevent hydrolysis of those imidosulphonates which, like the disodium salts, contain water of crystallisation, it is necessary to dry them slowly at a gradually rising temperature, and even then it is difficult to dehydrate them. Dipotassium imidosulphonate, the crystals of which are anhydrous, is particularly stable, and may be heated for hours at 140° or higher in undried air without the least sensible change; at 170—180°, however, it slowly fixes water and hydrolyses.

As the tripotassium imidosulphonate is much more soluble than the dipotassium salt, the latter dissolves readily in potassium hydroxide solution, from which it can be precipitated by carbonic acid (Raschig). Other and new reactions of the dipotassium salt observed by us are so similar to those we record of the sodium salt as to render it unnecessary to give them in detail.

Tripotassium Imidosulphonate.—Tripotassium imidosulphonate was prepared by Berglund, and again by Raschig, by dissolving the dipotassium salt in a solution of potassium hydroxide, evaporating, and crystallising.

Sodium Imidosulphonates.

Disodium Imidosulphonate.—Fremy's method for the preparation of the potassium salt is employed, but the details of working differ materially. Sodium nitrite as nearly pure as possible and sodium carbonate in crystals, in the proportion of 2 mols. of nitrite to 3 mols. (6 equivalents) of carbonate, mixed with twice their weight or more of water, are treated freely with sulphur dioxide in a capacious flask fitted with cork and gas tubes. After the carbonate crystals have dissolved, and the hydrogen carbonate precipitated and redissolved with continuous effervescence, the liquid, still quite alkaline to litmus, begins to grow warm, as it continues to absorb sulphur dioxide. To prevent any considerable rise of temperature, which might cause premature hydrolysis and spoil the operation, the flask is now kept cool by agitating in cold water, and the stream of sulphur dioxide somewhat moderated and carefully controlled. Neutralisation of the alkaline liquor by the sulphur dioxide is markedly retarded by the action of the nitrite, in the presence of which neutral sulphite cannot exist. When at length neutrality to lacmoïd paper is almost reached, the flask is actively agitated without intermission, the flow of gas greatly diminished, and then at once stopped, when the paper is just permanently reddened. The solution at this stage contains, besides a very little sulphate, nothing but the two salts nitrilosulphonate and metasulphite, which, omitting notice of intermediate stages, have been formed as follows:—

$$2NaNO_2 + 3Na_2CO_3 + 8SO_2 = 2N(SO_3Na)_3 + Na_2S_2O_5 + 3CO_2.$$

The apparently redundant metasulphite is necessary in order to get the nitrite converted wholly into nitrile salt. Its presence is almost equally essential for the preservation of the imidosulphonate about to be formed.

When complete neutrality is reached, or, perhaps, just passed, the solution, after a few minutes, suddenly becomes strongly acid and warm, and evolves much sulphur dioxide. Hydrolysis has occurred, but, owing to the presence of the metasulphite only through one stage, and the liquid now contains nothing but imidosulphonate, sulphate, and sulphur dioxide—

$$2N(SO_3Na)_3 + Na_2S_2O_5 + H_2O = 2HN(SO_3Na)_2 + 2Na_2SO_4 + 2SO_2.$$

Sulphurous acid appears to have no immediate hydrolysing action upon the imidosulphonate, but, as it would become oxidised to sulphuric acid, it must be removed. A rapid current of air is, therefore, passed through the liquid for half an hour or so, after which the addition of a very little sodium carbonate suffices to render it slightly alkaline and quite stable. It is now evaporated on the water-bath, so far as necessary, and then cooled to 0°, or a little below, when, in the course of some hours, most of the sulphate crystallises out. A second evaporation and cooling is generally needed to separate more of the sulphate, after which further evaporation and cooling to the ordinary temperature causes the separation of the disodium imidosulphonate in well-formed crystals. The mother liquor can be further worked for sulphate and imidosulphonate, if worth the trouble.

The reaction proves to be almost quantitative, for the salt obtained in crystals is 80 per cent., whilst there is considerable loss of salt in the mother liquors adhering to the very voluminous masses of sodium sulphate. The crude salt can be purified by recrystallisation from warm water, rendered slightly alkaline as a precaution against hydrolysis.

Instead of sodium carbonate, the equivalent quantity of normal sulphite, or of metasulphite, pure, and therefore freshly prepared, may be used along with the additional sulphur dioxide indicated by the equation already given. The mixture of nitrite and metasulphite becomes at once alkaline and rapidly heats up, so as to need cooling, in accordance with what has been stated. This mode of procedure is certainly less simple and less practicable than that described. It may also be mentioned that a sufficient excess of metasulphite will of itself convert all the nitrite to nitrile salt, but as, in that case, the addition of another acid is required to effect hydrolysis, the process does not give a good yield of imidosulphonate crystals.

It is not unfrequently convenient to prepare disodium imidosulphonate from the trisodium salt. The latter can be preserved without any special precautions, which is not the case with the disodium salt. Again, where the direct process for preparing sodium imidosulphonate has been carried out with impure salts, or if the proportions to be used, and other details, have not been rigidly adhered to, it may not be so easy to crystallise out the disodium salt, and here the very ready separation and purification of the trisodium salt becomes advantageous. From the trisodium salt, the disodium imidosulphonate can be prepared by treating the crystals with sulphuric acid slightly diluted, until neutrality to litmus is reached. The solution, with any crystalline precipitate (sulphate), is kept for some hours at or about 0°, and the mother liquor decanted, while still at that temperature, from the sodium sulphate. Evaporation, as already described, then yields the disodium salt in good crystals, pure, or almost so.

Disodium imidosulphonate crystallises readily in large, rhombic prisms. It is very soluble in water, slightly acid in reaction, and devoid of sulphurous taste. Its crystals, which contain water, do not effloresce, even in dry seasons, so that crystals of sodium sulphate among them may be easily recognised. In air kept dry by sulphuric acid, they slowly become opaque, but retain their shape, along with much of their lustre and hardness, whilst the rate of loss, even when they have been crushed, is so slow as to make a water estimation in this way almost impracticable. They can generally be kept for many weeks in bottles, and apparently for any time in a sufficiently dry atmosphere, but are liable to undergo hydrolysis into an acid mixture of sulphate and amidosulphonate. The solution of the salt is also unstable, but it may be heated for a short time to a moderate degree without change. The crystals can hardly be heated to 100° without some decomposition.

The decomposition of disodium imidosulphonate, which almost unavoidably attends the removal of the water of crystallisation, also complicates observation of the effects of a high temperature on it. For having been to some extent converted by this water into sulphate and amidosulphonate, it gives at first, when heated, only ammonia, coming from the reconversion of the amidosulphonate into imidosulphonate. But, at a higher temperature, this is followed by products the same as in the case of the dipotassium salt, namely, nitrogen with more than double its volume of sulphur dioxide, small brown and white sublimates, and sodium sulphate. The sodium salt appears to be much more fusible than the potassium salt, but then the latter was practically pure, whilst the former was mixed with the products of its hydrolysis, which must have affected its fusibility.

Disodium imidosulphonate in aqueous solution, like the far less soluble dipotassium salt (Berglund), does not give a precipitate with many of the usual metal salts. In moderately concentrated solution, however, it gives a precipitate of dipotassium imidosulphonate with solutions of potassium salts; of trisodium imidosulphonate with sodium hydroxide; and of a barium sodium imidosulphonate with barium hydroxide; concentrated ammonia solution also gives an abundant precipitate, which, when the disodium imidosulphonate is unmixed with other salts, consists of a sodium ammonium salt (p. 961); if, however, a little sodium nitrate, chloride, or other sodium salt is added before the ammonia, the latter, in concentrated solution, precipitates pure trisodium imidosulphonate. The two forms of precipitation are expressed by the respective equations :—

$$5HN(SO_3Na)_2 + 5NH_3 = 2Na_5(NH_4)N_2(SO_3)_4 + NH_4\cdot N(SO_3NH_4)_2,$$
$$HN(SO_3Na)_2 + NH_3 + NaNO_3 = NaN(SO_3Na)_2 + NH_4NO_3.$$

The precipitation by ammonia is in both cases greatly increased by excess of the reagent, and if the disodium imidosulphonate is added in powder to strong ammonia, much of the triammonium salt also precipitates.

Hydroxy-lead acetates, as was known, give copious precipitates. Normal lead acetate also gives a scanty precipitate of a lead imidosulphonate, even when the acetate is truly normal and the disodium salt in solution faintly acid to litmus (p. 969). Lead nitrate occasions no precipitate, but, unlike the acetate, it rapidly effects hydrolysis, and consequently precipitation of a little lead sulphate takes place.

Both mercury nitrates are also precipitating agents, acting here as they do when added in excess to a solution of trisodium imidosulphonate (p. 960). Mercuric oxide, especially the precipitated form, reacts with it to give mercuric disodium imidosulphonate (p. 980). Warmed with a moderately concentrated solution of the salt, the mercuric oxide dissolves, and, on cooling and standing, it deposits crystals of the double salt. Silver hydroxide is rapidly converted, by solution of disodium imidosulphonate, into the sparingly soluble silver disodium salt (p. 976). Cupric hydroxide is without action.

Evaporated on the water-bath with sodium carbonate, or even with the acetate, disodium imidosulphonate is partly converted into trisodium imidosulphonate, whilst carbon dioxide or acetic acid escapes. When acetate is used, therefore, there is the striking phenomenon of a strongly acid vapour rising from a liquid having a well-marked alkaline reaction.

In analysing the salt, we hydrolysed it by heating it with hydrochloric acid at 150° in sealed tubes for some hours, following Raschig's process for the analysis of the potassium salts. The composition of the salt is expressed by the formula $HN(SO_3Na)_2,2H_2O$, the results of analysis being—

		Found.			
	Calculated.	I.	II.	III.	IV.
Sodium	17·90	17·17	17·76	—	—
Sulphur....	24·90	—	—	24·88	24·78
Nitrogen ...	5·45	—	—	5·40	—

Trisodium Imidosulphonate.—This is prepared from the disodium salt by adding sodium hydroxide to its strong solution. It is unnecessary to have the disodium salt pure and in crystals. After following the process for getting this salt so far as to separate one good crop of sodium sulphate crystals, the solution is diluted with twice its volume, or more, of water, sodium hydroxide solution added, till it tastes slightly caustic, and then cooled in an ice-box. The trisodium salt begins to separate almost immediately after the addition of the sodium hydroxide, but the water previously added retards the separation, and allows the crystals to grow in the cooled liquid; in this way they can be better freed from the mother liquor. When collected and pressed on calico, the salt is almost pure, and can be rendered fully so by recrystallisation.

Trisodium imidosulphonate is easily prepared, and is a very stable salt. It forms thin, overlapping, hexagonal plates, which may grow to considerable size, but are seldom, if ever, to be seen single and perfect, or of very great thickness. The crystals readily effloresce in dry air, and have a mildly alkaline taste. The salt is sparingly soluble in very cold water, but very soluble in hot water, taking for dissolution at 27·5° about 5·4 parts of water. Its solution readily shows supersaturation. It is alkaline to litmus, and even to phenolphthaleïn, but has no action whatever on iodine solution; it is precipitated from its aqueous solution by alcohol without decomposition, and can be repeatedly recrystallised without any loss of alkali. Aqueous solutions are quite stable, even when boiled for a long time. The crystals melt when gently heated, and their water may be rapidly boiled off without causing any decomposition of the salt. In a vacuum over sulphuric acid, they lose only 11 mols. H_2O out of the 12 they contain. The salt loses more water when heated, but even at 160° it retains some, possibly through hydrolysis, so that, heated until decomposition begins, it always yields a very little water and ammonia (gas and sublimate). Heated in a vacuum, however, it yields even still less, so that atmospheric moisture seems to be active in hydrolysing it when heated in air.

The presence of hydrogen in the dried salt might have particular significance, since Fremy, and after him Claus, have represented the dipotassium salt as containing three atoms of hydrogen instead of the one given by the imide constitution and displaced by the metal in the normal salts. But careful combustion of some grams of the dried salt with copper oxide gave us in one case only 0·22 per cent., and in another only 0·24 per cent. of water, calculated from the hydrated crystals, and such a percentage corresponds to only about one-ninth of an atom, instead of the extra two, of hydrogen required by the sulphammonate constitution given by Claus.

When dried trisodium imidosulphonate is heated somewhat strongly in an open tube, it melts and effervesces, yields nitrogen and some sulphur dioxide, and sulphur which sublimes. The saline mass becomes also very dark coloured, from the presence in it of sulphur, and gradually solidifies, until at an incipient red heat it forms a semi-fused *hepar sulphuris*. By heating in a vacuum, proof is obtained that the sulphur dioxide comes only from the action of the air upon the sulphur. From 350° to 440°, gas of only very low tension is given off, along with sulphur vapour, forming a sublimate of drops. Just below the softening point of good soft lime-glass, the salt fuses and effervesces. The gas consists entirely of nitrogen. Some of the sulphur remains in the fused mass, partly free, partly as thiosulphate. A trace of sublimate of the ammonia compound with sulphur dioxide is formed. Apart from this, the reaction is expressed by the equation

$$2NaN(SO_3Na)_2 = N_2 + S + 3Na_2SO_4.$$

Acids readily dissolve trisodium imidosulphonate, yielding neutral solutions of the disodium salt when the quantity of acid is equivalent to one-third of the sodium. The action of concentrated sulphuric acid is remarkable; if it is not in excess, it dissolves the crystals, with marked fall of temperature, although if the quantity present is more than enough to form the disodium salt, heat is developed. From the neutralised solution, sulphate and disodium imidosulphonate can be crystallised out. Carbon dioxide also decomposes the trisodium salt in aqueous solution, sodium hydrogen carbonate being precipitated if the amount of water present is not too great. Concentrated ammonia precipitates the trisodium salt free from ammonia, and with its usual water of crystallisation. Ammonium salts suffer double decomposition with the trisodium salt, ammonia then becoming free by the decomposing action of water upon some of the triammonium salt. When concentrated solutions of the trisodium salt and of a potassium salt, such as the nitrate, are mixed, no change is observable, but on neutralising with an acid, the dipotassium salt is precipitated in crystals.

Trisodium imidosulphonate, unlike the disodium salt, precipitates many metallic salts, giving in some cases, however, only hydroxides. Precipitates of imidosulphonates are obtained with silver nitrate, the mercury nitrates, lead salts, and barium salts, whilst with calcium chloride crystals may slowly form which are of characteristic appearance. Specially noteworthy is the fact that silver nitrate added in different proportions yields three precipitates, distinct both in appearance and in composition. The compounds formed by these reagents are described later in this paper. Mercuric chloride has apparently no action upon trisodium imidosulphonate, for nothing separates, and the reaction to litmus remains alkaline. Mercuric oxide dissolves to a limited extent in solutions of the trisodium salt, more being dissolved in proportion to the trisodium salt, the weaker these solutions are; it makes them somewhat caustic (see in this connection, the reaction of mercuric disodium imidosulphonate with alkali hydroxide, p. 982).

It was not practicable to get the crystals of trisodium imidosulph-

	Calculated.	Found.		
		I.	II.	
Moisture..	1·00	43·66	43·56	Loss *in vacuo*.
11 mols...	42·70			
1 mol. ..	3·88	3·71	3·64	Loss at 110°.
		(0·23	0·27	Retd. at 110°).
Total	47·59	47·60	47·47	

onate completely dry for analysis, because the thin plates adhering together retained mother liquor, and, on the other hand, during much crushing and pressing with paper they effloresced. Avoiding the latter source of error, our results were $12\frac{1}{4}H_2O$, the $\frac{1}{4}$ representing 1 per cent. of moisture. The numerical details of the water determinations, which are a little complex, are given in the table, p. 960.

We have already given (p. 959) the percentage of retained water, as actually found in the salt dried with special care, as 0·22 and 0·24 per cent. The above numbers, 0·23 and 0·27, are difference numbers.

The analysis of the dried salt gave—

	Calculated.	Found.
Sodium..........	28·40	28·24
Sulphur..........	26·34	26·46
Nitrogen	5·76	5·92

The formula of the salt is therefore $NaN(SO_3Na)_2,H_2O + 11H_2O$.

Sodium Ammonium Imidosulphonate.

Possibly a salt two-thirds sodium and one-third imidosulphonate might be got in presence of an excess of the triammonium salt, but this is doubtful, because of the sparing solubility of the following salt in presence of ammonia, and because ammonia and another sodium salt convert disodium into trisodium imidosulphonate.

Pentasodium Ammonium Imidosulphonate.—This salt crystallises from dilute solution with 7 mols. H_2O, $Na_5AmN_2(SO_3)_4,7H_2O$, but from concentrated saline solution it crystallises with less water. To prepare the fully hydrated salt, strong ammonia solution is added in large excess to a solution of disodium imidosulphonate, which must be free from sulphate or other salt. Separation of the salt begins at once, or very soon, and continues for some time if the liquid is kept nearly ice-cold. It forms minute prisms, which bear moderate washing with concentrated ammonia, and can be drained on a tile, unchanged if under close cover. When dry, the salt does not smell noticeably of ammonia. The numbers obtained by calculation and experiment are as follows:—

	Calculated.	Found.
Sodium..........	18·95	19·19
Ammonium	2·97	2·85
Sulphur..........	21·09	20·95

A salt with $2\frac{1}{2}$ mols. H_2O only falls as a crystalline precipitate on adding strong ammonia to a solution of trisodium imidosulphonate and its equivalent at least of ammonium nitrate (3 mols.). Being but very little soluble in ammonia solution, it can be properly washed with this, and may then be drained on a tile under cover, without change. When heated, it loses water and ammonia without suffering aqueous fusion. It contains no nitrate. Analysis gave—

	Calculated.	Found.
Sodium	21·86	22·01
Ammonium.......	3·42	3·40
Sulphur...........	24·34	24·40

For notice of a monohydrogen sodium ammonium imidosulphonate, one in which the ammonium greatly predominates over the sodium, see p. 963.

Hydrogen Sodium Ammonium Imidosulphonate Nitrate.

On dissolving trisodium imidosulphonate and then its equivalent of ammonium nitrate (3 mols.) in half their combined weight of hot water in a closed, nearly full vessel, a cold solution is obtained, which sometimes remains supersaturated and unchanged, sometimes slowly deposits the trisodium salt of the ordinary form, but in thicker crystals. The attempt to redissolve the crystals by dipping the vessel in hot water readily succeeds, but is generally attended with the copious separation of some white opaque salt (sodium ammonium imidosulphonate ?). On the vessel being left for some days in a cold place with occasional agitation, the trisodium salt re-forms in crystals, and the opaque salt redissolves. When, however, the fresh mixed solution of the trisodium salt and ammonium nitrate in half their weight of water is placed in the steam-bath in an open glass capsule, ammonia freely escapes, and soon, groups of small prisms form, evidently in consequence of the loss of ammonia by the solution, and not its mere evaporation, for the addition of some water has little effect on the quantity of these crystals. The crystals could not be separated from their highly-concentrated mother liquor in a state fit for trustworthy analysis, but we are pretty confident of their being the salt now to be described.

A well-crystallised double salt of definite composition is obtainable by evaporating a solution of trisodium imidosulphonate with at least its equivalent of ammonium nitrate until the liquid is nearly neutral, then adding water to redissolve any crystals which have formed, and leaving the product to cool slowly. Throughout, care must be taken that the solution does not become acid during evaporation; this can be prevented by adding a drop or two of ammonia when necessary. In this way small, flat, thick prisms are obtained which are anhydrous and stable in the air. They cannot be washed, and must be freed from their mother liquor by pressure in paper. The composition of the new salt may be represented as being that of 1 mol. of diammonium imidosulphonate with 1 mol. of sodium nitrate. If a good excess of ammonium nitrate has been used, the crystals are almost pure, but hold a little water (*a*); with the use of less ammonium nitrate, the salt showed, on analysis, the presence of a very slight excess of disodium imidosulphonate. The yield of salt was three-fourths of the possible quantity. The mother liquor, on evaporation, gave crystals of sodium nitrate and some more of the salt. The double salt cannot be recrystallised, its solution yielding first good crystals of a salt which may be described as (anhydrous) diammonium imidosulphonate containing 3 per cent. of sodium, and, after this, crystals of the double salt. Since the mother liquor of the double salt yields sodium nitrate, it would seem that double decomposition occurs between sodium imidosulphonate and ammonium nitrate.

The presence of nitrate in the double salt cannot be directly indicated in the ordinary way, but may be at once detected by a new reaction of delicacy and of some general interest. The salt freely effervesces when immersed in strong sulphuric acid, the gas being nitrous oxide with a little nitrogen. No nitrosyl sulphate is produced. A very minute quantity of nitrate mixed or combined with an imidosulphonate can be detected by dropping the dry solid into a little of the acid, and not mixing them up too much. The reaction needs careful study. We ventured to determine the nitric acid in the salt by means of this reaction, taking the gas as nitrous oxide only, and got a good result, but do not feel justified in entering it in the tabular statement below.

In one preparation we determined the nitric acid; in the other it was undetermined, except in the experiment above referred to. The nitric acid was estimated by evaporating the salt with barium hydroxide to expel ammonia, filtering off the barium imidosulphonate, removing barium as carbonate, and then putting the concentrated solution of sodium nitrate into the nitrometer. The result was low, but that is hardly to be wondered at. Water, in that preparation in which it was present in any quantity, was estimated by heating the salt in dried air, and the result can be only approximate, for slight hydrolysis, with fixation of water, is hardly to be avoided.

	Calculated.	*a*.	*b*.
Sodium................	7·77	8·00	8·42
Ammonium............	12·16	11·71	11·37
Sulphur...............	21·62	21·62	22·08
Hydrogen nitrate.......	21·28	19·93	—

The preparation *a* was formed in presence of a good excess of ammonium nitrate, and *b* in presence of little more than enough of it. The calculation is for $HN(SO_3NH_4)_2,NaNO_3$.

Hydrogen Sodium Potassium Imidosulphonate Nitrate.

The very sparingly soluble dipotassium imidosulphonate is hardly affected by digestion with a cold dilute solution of sodium nitrate, and when dissolved in it by heating crystallises out again almost unchanged; if, however, it is left in a concentrated solution of sodium nitrate, it removes this salt from it. Taking about equivalent quantities of the salt, $HN(SO_3K)_2 : 3NaNO_3$, and leaving the solution of the nitrate standing over the powdery dipotassium imidosulponate in a loosely-covered beaker for some days, the latter gives place to a caked mass of crystalline granules, apparently homogeneous when seen under the microscope, but with no well-defined forms. The decanted mother liquor, evaporated a little, gives more of the granules, but no crystals of sodium or potassium nitrate. The granular mass, drained and pressed on a tile, has a composition closely approaching that of 1 mol. of dipotassium imidosulphonate to 1 mol. of nitrate, the potassium and sodium nitrates being in molecular proportion, $NaNO_3,KNO_3,2HN(SO_3K)_2$. It is decomposed by water, and is anhydrous.

	Calculated.	Found.
Sodium	3·32	3·61
Potassium..........	28·23	27·34
Sulphur	18·48	18·89
Hydrogen nitrate	18·20	18·01

The two potassium salts or the two sodium salts do not form double salts together. Disodium imidosulphonate and potassium nitrate suffer double decomposition. The formula of the salt just described shows also that, to some extent this double decomposition is reversible.

In our next communication we shall have to describe still more remarkable combinations of nitrates with oximidosulphonates.

Barium Imidosulphonates, Simple and Double.

Barium Imidosulphonate.—This salt has been prepared by Berglund, but no particulars of it have been published, except possibly in Swedish. It is obtained as a voluminous, coherent precipitate when trisodium imidosulphonate is added gradually to a solution of barium chloride kept in excess. When drained on a porous tile, after thorough washing, it is still very bulky, and hangs together in soft flocks, more like some organic salt than an inorganic barium salt. It retains moisture in the interstices of the matted masses of crystals with remarkable obstinacy, so that it cannot be made dry by draining on a porous tile or even in the desiccator except at the surface of these masses; yet it is not in the least deliquescent, and becomes dry in the air when spread out in very thin layers; indeed, in very dry air it is even slightly efflorescent. Analysis shows that it contains water, which it loses only very slowly even at 115°. Under the microscope, it is seen to consist of very long, slender, interlacing needles. It is only very slightly soluble in water, merely enough to cause the water to give a very slight opalescence with sulphuric acid. It is alkaline to litmus. It is decomposed a little by solutions of alkali carbonates. It may be dissolved in dilute nitric acid, and, with very rapid treatment, reprecipitated unchanged by barium hydroxide. This is a property which, with precautions, may be taken advantage of to remove sodium salt, which is nearly always present in the original precipitate, but always absent after second precipitation. Only once did we get the original precipitate free from sodium.

Analysis gave—

	Calculated.	Found.
Barium	48·38	47·91
Sulphur............	15·08	15·04
Nitrogen...........	3·29	3·31

The calculation is for $Ba_3N_2(SO_3)_4,5H_2O$. The alkalinity of the salt, measured by decinormal acid and methyl-orange, proved equal to one-third of the barium.

Ammonia added to a solution of the salt next described converts it into the insoluble tribarium imidosulphonate and ammonium imidosulphonate.

Barium Hydrogen Imidosulphonate.—This salt has been briefly noticed by Jacquelain and by Berglund. We have prepared it from the tribarium salt, entirely free from sodium, by cautious treatment with dilute sulphuric acid equivalent to slightly less than one-third of the barium, filtering off the barium sulphate formed, and evaporating in a desiccator, when minute, brilliant, orthorhombic crystals are obtained, moderately soluble in water. The salt is stable in the desiccator, or in the open air in dry weather, but soon hydrolyses in a bottle. In dried air, it is stable even when heated considerably, but it hydrolyses in ordinary air at 140°. Rapidly heated, it decomposes suddenly, giving a cloud of barium sulphate. Its solution is acid to litmus, but neutral to methyl-orange.

Proceeding in almost the same way as that followed by us

Woronin obtained apparently the same salt, but he assigned to it a molecule of ammonia more, calling it *barium sulphamate.* Since our preparation contains 1 mol. H_2O, the determination of barium and of sulphur agrees with both formulæ, $Ba(H_2NSO_3)_2$, "sulphamate," and $BaHN(SO_3)_2,H_2O$, imidosulphonate.

Quantitative analysis and the properties of the salt agree with the formula $BaHN(SO_3)_2,H_2O$.

	Calculated.	Found.	
		I.	II.
Barium..........	41·51	41·67	41·65
Sulphur..........	19·39	19·51	—

In warm solution, barium hydrogen imidosulphonate reacts with mercuric oxide to form the double salt.

Barium Ammonium Imidosulphonate.—By adding 1 mol. of barium hydroxide to 1 mol. of triammonium imidosulphonate ("neutral ammonium sulphamate"), Woronin observed the formation of a "soluble" barium salt with evolution of ammonia; he made no statement as to its composition. On adding barium hydroxide gradually to triammonium imidosulphonate until it nearly ceased to give a precipitate, we obtained a very sparingly soluble salt, which was found to be barium ammonium imidosulphonate. It was not fully analysed, but gave a percentage of barium of 41·87, whilst calculation for $BaNH_4N(SO_3)_2$ requires 41·64 per cent. But it is not improbable from what follows that it may have been a hydrous salt with less ammonia.

The experiment repeated with diammonium imidosulphonate gave us a precipitate at first gelatinous, but becoming granular after a time. Under the microscope, it was seen to consist of granular crystals intermixed with a very few slender needles of the tribarium imidosulphonate, insignificant in amount. Its alkalinity, determined by decinormal acid and methyl-orange, showed it to be a normal salt, the alkalinity being equal to one atom of univalent base to two atoms of sulphur present. After hydrolysis, the total ammonia, as well as the sulphuric acid, was estimated. The results agree with the calculation for $Ba_5(NH_4)_2N_4(SO_3)_8,8H_2O$, a five-sixths barium salt, corresponding, therefore, to the sodium ammonium salt.

	Calculated.	Found.
Barium	43·88	43·84
Sulphur............	16·40	16·53
Nitrogen	5·38	5·27

It is here assumed that the observed presence of a very little of the tribarium salt could be disregarded. The assumption that the preparation was the mixture $Ba_3N_2(SO_3)_4,5H_2O + 2[Ba(NH_4)N(SO_3)_2,1\frac{1}{2}H_2O]$ could not possibly be admitted as in accordance with the microscopic appearance of the preparation.

Jacquelain, by adding diammonium imidosulphonate to a slight excess of baryta water, obtained a precipitate which he very fully analysed, and found to have the empirical formula

$$(NH_3)_2(BaO)_2(SO_3)_3.$$

Instead of this impossible formula, we venture to write

$$Ba_4(NH_4)N_3(SO_3)_6,3H_2O,$$

the formula of an eight-ninths barium ammonium imidosulphonate, since the calculated numbers agree still better with his analysis than those for his formula.

	Calculated.	Found. (Jacquelain).
Barium	47·99	48·26
Sulphur............	16·81	16·81
Nitrogen...........	4·90	4·97
Hydrogen..........	0·88	0·88

Using an ammoniacal solution of barium chloride instead of baryta water, he got nearly the same results.

Barium Potassium Imidosulphonate.—This is a nearly insoluble crystalline salt, preparable by heating dipotassium hydrogen imidosulphonate with baryta water. It has been described by Berglund, and was known to Fremy. We have not analysed it, and believe it has not been analysed by others.

Barium Sodium Imidosulphonate.—When barium chloride in dilute solution is very slowly added, with constant stirring, to an excess of trisodium imidosulphonate, a crystalline precipitate is formed which under the microscope is seen to be free from any admixture of tribarium imidosulphonate. It is alkaline to litmus, very sparingly soluble in water, readily in nitric or hydrochloric acid, and decomposed by ammonium carbonate to a large extent, but never completely. It contains water, but does not noticeably lose weight even at 120°. Heated quickly to a higher temperature, it is dissipated in a cloud of barium sulphate. Five preparations made at different times show close agreement in composition, with the exception of that first prepared (which is entered in our note book as not pure). The numbers agree with those calculated for $Ba_{11}Na_8N_{10}(SO_3)_{20},13H_2O$, which may be written as $8BaNaN(SO_3)_2,H_2O + Ba_3N_2(SO_3)_4,5H_2O$.

	Calculated.	*a.*	*b.*	*c.*	*d.*	*e.*
Barium ..	41·12	42·35	40·05	41·17	40·45—41·07	40·85—40·91.
Sodium ..	5·02	5·08	5·26	4·93	—	5·25
Sulphur ..	17·46	18·80	—	—	17·54	17·56

The barium and sodium were determined by cautious ignition of the salt alone, then with sulphuric acid, and boiling out with water. The residue was weighed as barium sulphate, and the soluble matter, after re-ignition, weighed as sodium sulphate. The sodium of *d* was lost. The sulphur was estimated by hydrolysis, followed by precipitation with barium chloride, but the barium sulphate was here weighed in two quantities, that formed by hydrolysis and that by the barium chloride.

Calcium Imidosulphonates, Simple and Double.

Normal calcium imidosulphonate, $Ca_3N_2(SO_3)_4$, is not formed by the action of calcium chloride on sodium or ammonium imidosulphonate. When a solution of diammonium imidosulphonate is treated with pure, soft calcium hydroxide in the calculated quantity, ammonia is at once liberated and is all expelled by two or three evaporations of the solution to dryness. The salt left dissolves, and forms concentrated solutions crystallising in transparent prisms. But although the salt dissolves at first freely, the last portions are more difficult to bring into solution, and it may be that water partly decomposes the salt into the calcium hydrogen salt and calcium hydroxide. The salt was not analysed, except that a calcium determination was made, from which it appeared that the crystals have 10 mols. H_2O to 2 atoms of nitrogen in the salt.

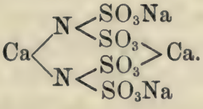
Calcium hydrogen imidosulphonate is obtained in radiating groups of fine needles when diammonium imidosulphonate and the calculated quantity of calcium hydroxide are mixed, and the solution repeatedly evaporated to expel all ammonia. The calcium hydroxide dissolves quickly after it is added. The salt is soluble, and has not been analysed.

Calcium ammonium imidosulphonate is a sparingly soluble salt, obtained when the calculated quantity of calcium hydroxide is dissolved in diammonium imidosulphonate solution, this quantity being in the proportion $Ca(OH)_2 : (NH_4)_2HN(SO_3)_2$. The salt rapidly crystallises after the dissolution of the lime. It has not been analysed.

Calcium Sodium Imidosulphonate.—To a hot concentrated solution of trisodium imidosulphonate a solution of calcium chloride is added, containing about the requisite quantity to form the tricalcium salt, and the mixture left to cool. It is not the tricalcium salt, however, but the calcium sodium salt, which crystallises out in groups of hard, brilliant prisms; it can be recrystallised, and thus purified if necessary. It is sparingly soluble in cold water, and has an alkaline reaction. It only very slowly takes up carbonic acid from the atmosphere. Analysis corresponds to the composition $CaNaN(SO_3)_2,3H_2O$.

		Found.		
	Calculated.	I.	II.	III.
Calcium....	13·75	13·95	14·07	—
Sodium....	7·90	7·72	—	—
Sulphur....	21·99	—	22·21	—
Nitrogen...	4·81	—	—	4·88

The relative positions of the calcium and sodium are not very certain. For sake of symmetry, the sodium might be put in the imide relation, but such a procedure has nothing to support it. Taking the sodium to act as the more basylous element, the formula becomes



Lead Imidosulphonates.

A lead imidosulphonate was used by Jacquelain, and again by Berglund, to prepare imidosulphonic acid; but we know of no publication of particulars concerning the salt employed.

Disodium or other bibasic imidosulphonate does not yield a precipitate with lead nitrate, and only a very slight one with normal lead acetate. It is therefore necessary to take either the trisodium imidosulphonate, or to employ a basic lead acetate, in order to get an insoluble lead salt in sufficient quantity. This salt is always a basic or hydroxy-salt; so that its separation renders the mother liquor much less basic than the mixed solutions employed. Hence the retention of lead salt and imidosulphonate together in the mother liquors, and also the fact that either one or the other must be present in them. In fact, it is only by using a basic lead acetate that it is possible to throw all the imidosulphonate out of solution, whilst to precipitate all the lead, it is necessary to use the trisodium salt. Hydroxy-lead acetate, and lead nitrate or normal acetate yield precipitates of different salts with trisodium imidosulphonate, but the metal in the salt precipitated consists entirely of lead. One other point to be here noticed, as affecting precipitation, is the solubility in solution of normal lead acetate of the lead imidosulphonates insoluble in water. The solution is alkaline, and freely precipitable by carbonic acid, and may be regarded as containing basic lead acetate and the soluble lead hydrogen imidosulphate. Although a superficial examination of the reactions of imidosulphonates with lead salts may suggest the view of their being ill-defined, fuller investigation proves them to be quite definite.

The *normal salt*, $Pb_3N_2(SO_3)_4$, appears not to exist. The first addition of lead acetate or nitrate gives a precipitate of a basic salt with trisodium imidosulphonate; and basic lead imidosulphonate, treated with small quantities of nitric acid, dissolves, as a whole, to yield a neutral or slightly acid solution, the undissolved part remaining unchanged (p. 971).

The *lead hydrogen salt*, $HN(SO_3)_2Pb$, appears to exist in solution, but the attempt to separate it leads to decomposition. Its solution can be prepared by treating either basic salt with somewhat less than enough dilute sulphuric acid, and decanting the clear solution from the sulphate and undecomposed basic salt. The solution can be preserved unchanged, in absence of acetates, for a very short time only. It is slightly acid to litmus. Left in a desiccator, it suffers decomposition into amidosulphonic acid and lead sulphate, slowly at first, but more rapidly as the solution grows concentrated. Heating the solution effects the same change. Alcohol produces a voluminous precipitate, gradually giving place to a crystalline deposit which partly adheres to the sides of the vessel, is nearly insoluble in water, and appears to be sulphate.

Hemihydroxy-lead Imidosulphonate, $HOPbN(SO_3PbOH)_2$.—When lead nitrate and trisodium imidosulphonate in solution are brought together in widely varying proportions, this salt is precipitated, voluminous at first, but soon becoming dense and granular. Disodium imidosulphonate and sodium nitrate are the other products of the reaction

$$3Pb(NO_3)_2 + 3H_2O + 4Na_3N(SO_3)_2 = (HOPb)_3N(SO_3)_2 \\ + 3HNa_2N(SO_3)_2 + 6NaNO_3.$$

The precipitation is very nearly quantitative. If the trisodium salt is not used in excess, the mother liquors are neutral to methyl-orange.

Normal lead acetate may be used in place of the nitrate, but the results are not so satisfactory. The best way to proceed is to mix the solutions rapidly together in something approaching the right proportions; or the two salts may be rubbed together in the solid state and then treated with water. By either of these methods, if the proportion of either salt is not very many times greater than it should be, a product of constant composition is obtained, which differs, however, from the pure lead salt in having about $\frac{1}{73}$rd of the lead replaced by hydrogen. The weight of the precipitate obtained from a given quantity of trisodium salt is greater with lead acetate than with the nitrate, and greater as the excess of acetate used is greater. The acetate mother liquor, though alkaline to methyl-orange, is acid to phenolphthaleïn, and, after the lead in it is replaced by sodium, by precipitation with normal sodium oxalate, can be titrated by sodium hydroxide, using phenolphthaleïn as indicator. Thus tested, these liquors proved to contain free acetic acid; the quantity increasing with that of the acetate used, and, therefore, with the precipitate produced. In these experiments, particularly good *normal* lead acetate was used. It appeared from the experiments made that about one-eighth of the excess of lead acetate used must react with disodium imidosulphonate, a product of the main reaction as already pointed out, the change being as follows:—

$$3Pb(OAc)_2 + 3H_2O + HNa_2N(SO_3)_2 = (HOPb)_3N(SO_3)_2 + 2NaOAc + 4HOAc.$$

The acetic acid thus generated acting so as to reverse the reaction, is probably the cause of the very slight replacement of lead by hydrogen in the salt precipitated by acetate.

When the trisodium imidosulphonate solution is added by degrees to the lead acetate, a gelatinous precipitate, like lead hydroxide, forms and then redissolves in the lead acetate. When enough of the sodium salt has been added to cause a permanent precipitate, this is somewhat slimy, and only slowly becomes pulverulent, whilst the walls of the vessel get coated with a crystalline precipitate. The mixed product is unfit for analysis. When the lead acetate is added gradually to the sodium imidosulphonate, the precipitate also remains voluminous and somewhat gelatinous, and is probably not a pure product. If too much of the sodium salt has not been added, and the solution is quickly filtered, it slowly yields a few brilliant crystals of what is evidently, both from its appearance and the results afforded by an imperfect analysis, the hydroxy-lead salt.

The hydroxy-lead salt, in perfect, brilliant, microscopic prisms, can be obtained very pure by treating the more basic lead salt, next described, with but little more nitric acid than is required to remove the excess of lead. The nitric acid can be clearly seen to dissolve a portion of the more basic salt, and almost at once to deposit a crystalline precipitate and incrustation of the hemibasic salt. If, instead of stopping the addition of nitric acid when enough has been used, more is added, the crystalline salt proportionately dissolves without reprecipitating. The nitric solution is neutral to methyl-orange, so that, in the dissolution of the more basic salt, the reaction is

$$(HOPb)_3N(SO_3)_2,Pb(OH)_2 + 6HNO_3 = HPbN(SO_3)_2 + 5H_2O + 3Pb(NO_3)_2,$$

and then, this solution reacting with a further quantity of the more basic salt, gives

$$2(HOPb)_3N(SO_3)_2,Pb(OH)_2 + HPbN(SO_3)_2 = 3(HOPb)_3N(SO_3)_2 + H_2O.$$

This, in a manner, can be shown by pouring the nitric solution into a large excess of hydroxy-lead acetate solution, when the hemi-hydroxy-lead imidosulphonate also precipitates in the pure state. There is also the fact observed that the nitric solution when soon poured off from the undissolved basic salt, contains much lead, whereas if it is left over the undissolved basic salt it goes on depositing a crystalline precipitate of the hemi-basic salt.

The modification of this process, expressed by the equation

$$3(HOPb)_3N(SO_3)_2,Pb(OH)_2 + HN(SO_3Na)_2 + 2HNO_3 = \\ 4(HOPb)_3N(SO_3)_2 + 2NaNO_3,$$

has also been successfully carried out by adding the nitric acid very slowly and shaking well.

The hemi-hydroxy-lead imidosulphonate is an anhydrous salt, not counting its hydroxyl, very permanent, losing nothing at 100°, insoluble in water, and scarcely, if at all, alkaline in reaction when in contact with wet litmus paper.

A number of preparations by different methods have been analysed with closely concordant results:

	Calculated.	Found.
Lead..........	73·40	73·21—73·35
Sulphur	7·56	7·50

The lead acetate precipitates gave from 72·31 to 72·78 per cent. lead, and from 7·52 to 7·65 per cent. sulphur. The sodium was determined in some of these preparations, and was found to be no more than 0·075 per cent.

The pure salt was also titrated with a standard nitric acid, and its basicity found to agree with that calculated. In order to just dissolve 1 gram of the salt leaving the solution neutral to methyl-orange, 48·71 c.c. of the acid was required, the calculated being 47·28 c.c.

Five-eighths Oxy-lead Imidosulphonate, $(HOPb)_3N(SO_3)_2,PbO$ *or* $Pb(OH)_2$.—This salt is precipitated on adding trisodium imidosulphonate to excess of basic lead acetate, the quantity of basic lead acetate needed being very large; it is advantageous to use not less than 6 mols. of hemi-hydroxy-lead acetate to 1 mol. of trisodium imidosulphonate. The calculated quantity is 5 mols., but an excess helps to keep sodium out of the salt. The reaction is as follows:—

$$Na_3N(SO_3)_2 + 5HO{\cdot}Pb{\cdot}OAc = (HOPb)_3N(SO_3)_2,Pb(OH)_2 \\ + 3NaOAc + Pb(OAc)_2,$$

and, therefore, it would be better probably to employ a more basic lead acetate. Using, as we did, about 6 mols. of hemi-hydroxy-lead acetate, the mother liquor, after precipitation, was still markedly basic. Both precipitate and mother liquor were quite free from sulphate; a very little sodium was found in the precipitate after it had been well washed, but no acetic acid. It is insoluble in water, but readily soluble in dilute nitric acid. Its partial dissolution in nitric acid leads to the formation of the hemi-hydroxy-lead imidosulphonate. It has scarcely any action on moist, red litmus, when left in contact with it. It is insoluble in solutions of the parent salts, and is not altered by them.

It does not lose water even when heated to 130°, but, at a higher temperature, it gives off, first water, then ammonia, then water again, then it blackens through formation of sulphide, and finally it evolves sulphur dioxide. The loss of water and ammonia is explained by the equation

$$3(HO)_5Pb_4N(SO_3)_2 = 6PbO + 3PbSO_3 + 3PbSO_4 + NH_3 + N_2 + 6OH_2.$$

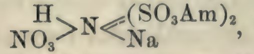
Then the lead sulphite becomes, as usual by the rising temperature, partly lead sulphide and sulphate, partly lead oxide, and sulphur dioxide. At the temperature of fusion, the sulphide and oxide would, of course, react.

Two preparations were analysed, *a* and *b*:

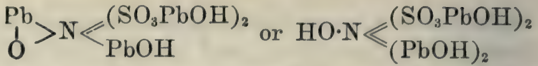
	Calculated for $(HOPb)_3N(SO_3)_2,PbO,\frac{1}{2}H_2O$.	Found. *a*.	*b*.	*c*.
Lead............	76·81	76·79	76·05	76·82
Sulphur.........	5·94	5·82	6·00	—
Sodium	—	0·15	0·15	—

Behaviour of Imidosulphonates as Compound Amines towards other Bodies.

We have here collected some facts, already recorded in the paper, which appear to show that imidosulphonates form compounds in which the nitrogen becomes quinquevalent as in ammonium salts.

First, in order of observation, there is the retention of 1 mol. of water at 110° by the trisodium salt. The potassium salt, which crystallises with 1 mol. H_2O (Raschig), has not been examined in this respect. Next, there is the union of the diammonium salt with sodium nitrate to form a well-crystallised compound, which may be formulated as  $\begin{smallmatrix}H\\NO_3\end{smallmatrix}{>}N{<}\begin{smallmatrix}(SO_3Am)_2\\Na\end{smallmatrix}$, and the similar compound of dipotassium imidosulphonate. Lastly, there is the more basic lead salt described in the last part of the previous section of this paper.

This may be written



$\begin{matrix}\mathrm{Pb}\\|\\\mathrm{O}\end{matrix}\!>\!\mathrm{N}\!<\!\begin{matrix}(\mathrm{SO_3PbOH})_2\\\mathrm{PbOH}\end{matrix}$ or $\mathrm{HO{\cdot}N}\!<\!\begin{matrix}(\mathrm{SO_3PbOH})_2\\(\mathrm{PbOH})_2\end{matrix}$

according as we reject or admit the presence of 1 mol. of water, as shown by analysis.

Silver Imidosulphonates.

Silver nitrate and trisodium imidosulphonate yield three different compounds, in which 1, 2, and 3 atoms of sodium are replaced by silver. Such an unusual behaviour in the salt of a polybasic acid gives to imidosulphonic acid a special interest.

The addition of silver nitrate in limited quantity causes a white precipitate which redissolves to be rapidly followed, unless the solutions are very dilute, by the separation of another compound. This consists of interlacing, fibrous crystals, filling the liquid as a felted mass, even when the quantity present is small.

The addition of more silver nitrate to the liquid and crystals, generally causes more of the first white precipitate to be formed, and subsequently, if sufficient of it is added, the disappearance of both the precipitates together. The new solution becomes almost immediately full of a third precipitate, this time of very dense, hard, minute, separate crystals, which rapidly subside as a deposit, in appearance closely resembling silver sand. A salt of the same composition as this often occurs as a hard, crystalline incrustation on the sides and bottom of the beaker when a little silver nitrate is added to the mother liquor from the felted crystals.

Some experiments with tripotassium imidosulphonate have given us salts apparently analogous to those got from the sodium salt, but we have not further examined them.

*Triargentic Imidosulphonate.**—By adding the sodium salt in limited quantity to silver nitrate, the white precipitate is also formed, and is now permanent in contact with the mother liquor. This precipitate, which is triargentic imidosulphonate, is but very slightly soluble in water, and, after long washing on the filter, yields a milky filtrate. It is a relatively voluminous precipitate, forming chalk-like masses when dry. It is without water of crystallisation, as was to be anticipated, but even when heated for a long time at 110° retains 0·55 per cent. of water (possibly fixed by hydrolysis from the atmosphere), as determined by combustion with copper oxide. It bears heat well, but at a comparatively high temperature it rapidly decomposes with or without fusion, giving in the open tube first a very little ammonia and a slight sublimate, then sulphur dioxide, nitrogen, silver, silver sulphide, and silver sulphate. When heated in a vacuum, scarcely any sublimate is formed, and no change takes place till the temperature reaches 440°, when gas comes off, and blackening without fusion occurs; the residue consists of silver sulphate, silver sulphide, and silver, and the gas of nitrogen and sulphur dioxide. The proportions of these products vary a little, a higher temperature apparently giving more silver and sulphur dioxide. The first moiety of gas was thus found to consist of 4 vols. of nitrogen to 5 vols. of sulphur dioxide, and the second moiety of 2 vols. of nitrogen to 3 vols. of sulphur dioxide, so that the decomposition lies between those expressed by the equations

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* May possibly have been already described by Berglund in the *Lunds univ. Arsk.*, **12**.

$$4AgN(SO_3Ag)_2 = 2N_2 + 2SO_2 + 5Ag_2SO_4 + Ag_2S,$$
$$\text{and } 4AgN(SO_3Ag)_2 = 2N_2 + 4SO_2 + 4Ag_2SO_4 + 2Ag_2,$$

but nearer the first one.

The salt was prepared for analysis by adding the sodium salt gradually, with stirring, to excess of silver nitrate. In spite of the strongly alkaline reaction of the former, the mother liquor of the precipitate proved to be neutral, as it should be; the precipitate was brilliantly white, without the slightest brown tinge. As it is not decomposed by water, it was well washed. Its analysis gave, besides the 0·55 per cent. water mentioned above, the following results:—

		Found.		
	$AgN(SO_3Ag)_2$.	I.	II.	III.
Silver..........	65·06	64·92	64·53	64·58
Sulphur........	12·85	—	—	12·94
Nitrogen.......	2·81	—	—	3·16

Diargentic Sodium Imidosulphonate.—The sandy precipitate, described above, is a salt with 2 atoms of silver to 1 atom of sodium. It is sparingly soluble in water, and very slightly decomposed by it, silver hydroxide being one of the products. It is of a faint buff colour. Under the microscope its crystals are seen to be hexagonal plates, always single; they act on polarised light. This salt, though otherwise anhydrous, retains a little water with the same firmness as is shown by the other silver salt; its behaviour when heated also closely resembles that of the latter, except that, naturally, sodium sulphate forms part of the residue as well as silver sulphate.

To prepare the salt for analysis, the sodium salt was added gradually to a little less than two-thirds of its equivalent of silver nitrate. The sandy precipitate obtained was only slightly washed, and then drained and dried on a tile. An incrustation (washed *in situ*) was also analysed. The results were:—

	$Ag_2NaN(SO_3)_2$.	Incrust.	Precip.
Sodium	5·57	5·61	5·67
Silver	52·30	52·02	51·87
Sulphur	15·50	—	15·60
Nitrogen	3·39	—	3·45

Argentic Disodium Imidosulphonate.—This salt, which forms crystalline fibres, is the most soluble of the three salts, but is still only sparingly so. It is gradually and visibly decomposed by water, the change consisting, apparently, partly in the formation of silver hydroxide and hydrogen disodium imidosulphonate, partly in resolution into trisodium salt and the diargentic sodium salt. On this account, although readily produced, it is difficult to get pure. It retains a very little water, as usual, and behaves when heated almost like the preceding salt. For analysis, it was freed from mother liquor by pressure in a calico filter, and then between porous tiles. In preparing it, the sodium salt was added to a little less than one-third of its equivalent of silver nitrate, and the mixture agitated at once in order to redissolve the white precipitate of silver salt first thrown down, and before the fibrous crystals begin to form. Analysis gave:—

	$AgNa_2N(SO_3)_2$.	a.	b.	c.	
Sodium	14·02	14·75	—	—	13·81
Silver	32·93	33·07	33·49	33·50	33·49
Sulphur	19·51	—	19·18	19·52	—
Nitrogen	4·27	—	—	4·29	—

Double Mercury Imidosulphonates.

Single mercury imidosulphonates seem to be incapable of existence.

Mercury Potassium Imidosulphonates.—Berglund prepared mercury dipotassium imidosulphonate, $HgN_2(SO_3K)_4$, from tripotassium imidosulphonate. We have prepared it from dipotassium imidosulphonate by adding mercuric oxide to it, heating the mixture with water, filtering hot if necessary, and leaving the solution to cool. The salt, which is nearly insoluble in cold water, separates out in very minute needles, sometimes arranged loosely, sometimes in spherical tufts, and is, when dry, of silvery lustre.

An *oxymercuric potassium salt*, analogous to the sodium salt (p. 983), seems to be among the products of the reaction between mercuric nitrate and potassium imidosulphonates, but we have not made any study of it.

The behaviour of mercury dipotassium imidosulphonate with acids, as observed by us, is of interest in connection with the theory of the constitution of these salts, and we shall refer to it later on when discussing that point (p. 986). When the salt, in the form of paste with water, is treated with nitric acid, it is converted into the very slightly soluble dipotassium imidosulphonate, all its mercury dissolving as mercuric nitrate. When washed and drained on a tile, the salt left undissolved was found to be free from mercury and from sulphate. The same experiment can be carried out by the use of dilute sulphuric acid, but less satisfactorily. The nitric acid used may be strong and in excess, but the sulphuric acid must be dilute and not in excess, and is apt to give a small precipitate of mercuric salt. Hydrochloric acid removes both metals, and causes extremely rapid hydrolysis.

Mercury Barium, $HgN_2(SO_3)_4Ba_2$, *and other Double Mercury Imidosulphonates.*—According to Berglund, mercury dipotassium imidosulphonate gives a series of double salts in which the potassium is replaced by another metal. It follows that these salts can also be prepared from the mercury sodium salts, but we have only made ourselves familiar with the mercury barium salt, particularly noticed by Berglund. It is a lustrous, crystalline, dense salt, almost insoluble in cold water.

Mercury Dihydrogen Imidosulphonates.—When mercury barium imidosulphonate is treated with dilute sulphuric acid, not more than sufficient to remove the barium, it appears to be sharply converted into barium sulphate and mercury hydrogen imidosulphonate. This observation of Berglund's we have confirmed and extended. We worked quantitatively, and were careful to use the sulphuric acid in slight deficit, and to filter quickly. But, on testing the filtrate, we found the hydrolysis of the imidosulphonate into sulphate and amidosulphonic acid had already begun. It progressed steadily, and in 10 minutes a good deal of sulphuric acid had been formed, showing that mercury hydrogen imidosulphonate is even less stable than hydrogen imidosulphonate itself. In about 10 minutes also, the solution began to grow turbid, from separation of an oxymercuric salt, probably amidosulphonate. The fresh solution, when almost neutralised with potassium hydroxide, gave a slight, white turbidity, doubtless of oxymercuric potassium imidosulphonate; this dissolved when a little more alkali was added. The slightly alkaline solution, thus prepared, soon began to deposit minute crystals, which we identified as mercury dipotassium imidosulphonate. Thus, we had proved, so far as might be done, that the fresh filtrate from the barium sulphate is really a solution of mercury hydrogen imidosulphonate.

Oxymercuric Hydrogen Imidosulphonate.—A second salt of mercury and hydrogen can be readily obtained which is at once both basic and acid, as its name indicates. Highly concentrated mercuric nitrate solutions, even when as free as possible from nitric acid, dissolve solid potassium or sodium imidosulphonates, yielding clear and comparatively stable solutions. When these solutions are heated, the imidosulphonate hydrolyses into amidosulphonate, but if diluted without heating they deposit oxymercuric hydrogen imidosulphonate. The same salt is almost immediately precipitated when trisodium imidosulphonate in solution is added to mercuric nitrate.

To prepare this salt, about 5 parts by weight of an undiluted mercuric nitrate solution are taken, equal to about half its weight of mercuric oxide, and into it, with stirring, is poured a cold solution (necessarily dilute) of 1 part of trisodium imidosulphonate; precipitation of the salt begins almost at once, and is finished in a few minutes. The mother liquor still contains much mercuric nitrate and some imidosulphonate, besides sodium nitrate and much nitric acid. The addition of a little more trisodium salt causes scarcely any further precipitation, but a larger quantity throws down the oxymercuric sodium salt. The brilliant white and voluminous oxymercuric hydrogen salt hydrolyses only very slowly in its acid mother liquor, on account of the protective action of the mercuric nitrate. It should be repeatedly washed by subsidence and decantation with abundance of cold water, and drained till dry on a tile or filter. If less mercuric nitrate has been used, and the precipitate contains sodium (as oxymercuric sodium salt), this may be converted into the pure oxymercuric hydrogen salt either by digestion for a day with concentrated mercuric nitrate solution and washing, or simply by continued and thorough washing with water. If digestion with mercury nitrate solution is adopted, the water used for the first washing must contain a little nitric acid to guard against the formation of any oxynitrate.

Oxymercuric sodium imidosulphonate, when washed with much water for a long time, leaves a far smaller weight of oxymercuric hydrogen salt, and imparts continuously to the wash-waters small quantities of a mercury sodium imidosulphonate, apparently the same as that got by digesting mercuric oxide in a solution of mercuric disodium imidosulphonate, perhaps $O[HgN(SO_3Na)_2]_2$. These washings are neutral or faintly alkaline, and when evaporated a little on the water-bath, yield small quantities of micaceous crystals. This reaction appears to be expressed by the equation—

$$2Hg(OHgSO_3)_2NHgN(SO_3Na)_2 + H_2O = O[HgN(SO_3Na)_2]_2 + 2HN(SO_3HgO)_2Hg.$$

Oxymercuric hydrogen imidosulphonate is an anhydrous salt.

After drying in a desiccator, it loses 0·7 to 0·8 per cent. of water when heated at 100° or above. It may be heated in dried air to 180° or higher without changing; but at a little below a dull red heat it decomposes, and then slowly gives off water, nitrogen, and sulphur dioxide; at this temperature it is yellow, but when cooled it again becomes white. At the softening point of hard glass, it melts to a dark red liquid, and effervesces, yielding sublimates of metallic mercury, mercurous and mercuric sulphates, and some other mercuric salt not sulphate and apparently nitrogenous. It seems impossible, even in a vacuum, to decompose it completely before the mercury sulphates themselves partly decompose. The gas first given off consists of nitrogen with half its volume or more of sulphur dioxide; subsequently it consists of nitrogen, sulphur dioxide, and oxygen. When rapidly raised to a red heat, the salt, at the moment of melting, effervesces and decomposes almost explosively.

Its reactions with sodium hydroxide and chloride, and with trisodium imidosulphonate are similar to those of the oxymercuric sodium salt (p. 984). Its basic or oxy-salt character is thus clearly demonstrated, independently of the evidence derived from analysis. The presence of hydrogen, other than that of hydration, is shown by first heating the salt for some hours at 180° in a current of dried air, and then to a much higher temperature, when water vapour, containing sulphuric acid, is given off. As the salt would yield only a little more than one-thousandth of its weight of hydrogen, and the isolation of the water would be difficult, hydrogen was not quantitatively estimated. The analytical results obtained were—

	$HN(SO_3)_2Hg_3O_2$.	(*a.*)	(*b.*)
Mercury	74·35	74·03	74·09
Sulphur	7·93	8·06	8·00
Nitrogen	1·73	1·76	1·65
Hydrogen........	0·12	—	—
(Sodium)	—	0·06	0·06
(Moisture)	—	0·20	0·13

The preparation *a* was made by the direct method; the other, *b*, was digested with mercuric nitrate to remove the sodium which it contained, and then washed with water slightly acidified with nitric acid.

On writing down the reaction by which this salt is formed from mercuric nitrate and trisodium imidosulphonate—

$$3Hg(NO_3)_2 + Na_3N(SO_3)_2 + 2H_2O = HN(SO_3)_2Hg_3O_2 + 3NaNO_3 + 3HNO_3,$$

and comparing it with the equation where oxymercuric sodium imidosulphonate is the product, it will be seen that in both cases the nitrate comes out half as sodium nitrate and half as nitric acid, and that the oxymercuric hydrogen salt may be represented as resulting from the reaction of the sodium salt with mercuric nitrate, thus:—

$$Hg(NO_3)_2 + NaN(SO_3)_2Hg_2O + H_2O = HN(SO_3)_2Hg_3O_2 + NaNO_3 + HNO_3.$$

Now, this reaction can actually be realised, as already stated, but only with difficulty and in presence of great excess of mercuric nitrate solution, active probably by virtue of its free acid. In the direct method of preparing the hydrogen salt, it is formed simultaneously with half as much again nitric acid as is produced when the sodium salt is formed. From this it would appear that there is a point where, if the nitric acid is in sufficient quantity along with the mercuric nitrate, nitrogen takes or keeps hydrogen in place of mercury, and the second half of the sulphonic radicles, as well as the first, takes mercuric oxide in place of sodium, just as it does in other cases even in presence of free acid; this, however, is difficult to determine by direct experiment with nitric acid, because of its liability to cause hydrolysis after a time, and of the uncertainty in knowing when the change sought for has occurred.

Mercury Sodium Imidosulphonates.—There are two mercury sodium imidosulphonates. The monosodium salt is oxymercuric or basic, but the disodium salt is normal, and corresponds in composition with the potassium salt obtained by Berglund.

Unless gradually added to the solution of trisodium imidosulphonate, mercuric nitrate causes, almost immediately, a white, flocculent, crystalline precipitate, but this disappears on agitation so long as there is enough of the sodium salt remaining to keep the mixture alkaline or neutral; when, however, this point is passed, the precipitate is permanent, and consists of *oxymercuric sodium salt.* If the nitrate is added till neutrality is just reached, or nearly reached, the solution soon begins to deposit small, brilliant crystals, or does so after some evaporation. These are *normal mercuric disodium imidosulphonate.* The addition of a solution of trisodium imidosulphonate to one of mercuric nitrate, free from any unnecessary excess of nitric acid, produces, as already stated, a white crystallo-flocculent precipitate which, if sufficient excess of nitrate remains, is the *oxymercuric hydrogen salt;* if there is too little nitrate, some oxymercuric sodium salt will be deposited as well.

Mercuric Disodium Imidosulphonate.—There is little to add concerning the preparation of this salt from the trisodium salt. Here, as in other cases, it is better to have the mercuric nitrate solution highly concentrated, as then there need be but little excess of nitric acid.

To prepare this solution, moderately concentrated nitric acid is so far saturated with mercuric oxide that oxynitrate begins to form; it is then decanted from the excess of oxide and left to clarify by subsidence. If too much mercuric nitrate has been added to the sodium salt, the proportions can be successfully rectified by adding more sodium salt. The mercuric disodium salt can be purified, if necessary, by recrystallisation from hot water. Mercuric disodium imidosulphonate can also be readily prepared from disodium imidosulphonate and mercuric oxide. The two substances are triturated together in about the right proportions mixed with water, and warmed with it; the solution is then filtered, if necessary, and set aside to crystallise.

Mercuric disodium imidosulphonate crystallises in small, brilliant prisms always separate, quite permanent in the air, and sparingly soluble in cold water; the solution has a neutral reaction. The crystals contain 6 mols. H_2O, of which only four are lost in a vacuum at the ordinary temperature.

If heated at 100°, after exposure in a vacuum desiccator, it loses most of the remaining water, but not all, for then (and at higher temperatures, as 130°, more quickly), it increases slowly in weight by fixing atmospheric moisture, and becomes hydrolysed and strongly acid (see effects of heating dipotassium imidosulphonate, p. 954). If heated more strongly in an open tube, it yields a small sublimate of an ammonia-sulphite salt, mercurous sulphate, and mercury, sulphur dioxide and nitrogen being given off, and mercurous, mercuric, and sodium sulphates left as a residue.

When heated slowly in a Sprengel vacuum, it suffers change in a way that can be more closely studied. Even at 444°, no material alteration takes place, but just below a red heat it decomposes steadily, temporarily blackening through formation of mercuric sulphide, and giving besides much mercury as a sublimate, nitrogen and sulphur dioxide in the proportions of two volumes of the former to three of the latter, and a little very volatile white ammoniacal sublimate, together with a very little water, and another white sublimate volatilising again at 350—400°. The residue is sodium sulphate. That margin of the white sublimate which is more remote from the heat consists of mercurous sulphate, but the nature of the rest, which adheres firmly to the glass, is but imperfectly made out. It is a mercury compound scarcely affected by potassium hydroxide, boiling water, or dilute nitric acid, and seems to be a derivative of mercuric sulphate containing nitrogen.

The main changes by heat appear to be—

$$2HgN_2(SO_3Na)_4 = 4Na_2SO_4 + HgSO_4 + HgS + 2SO_2 + 2N_2,$$

and then on further heating—

$$4Na_2SO_4 + 2Hg + 4SO_2 + 2N_2.$$

The ammoniacal sublimate and moisture are evidently due to water retained by the salt, probably through hydrolysis; whilst the mercurous sulphate is formed from mercury and mercuric sulphate.

With solutions of ordinary metallic salts, the mercuric disodium salt gives the various double mercury imidosulphonates noticed by Berglund. For example, with barium chloride it gives a precipitate of mercury barium imidosulphonate.

Sodium hydroxide precipitates mercuric oxide from the pure salt, but not in the presence of sodium imidosulphonate, and under any circumstances the precipitation of the mercury is far from complete. According to Raschig, Berglund found that mercuric dipotassium imidosulphonate gave no precipitate with potassium hydroxide, but in this respect we find that the potassium salt behaves like the sodium salt, except that the precipitate is perhaps smaller. Dilution lessens precipitation (see behaviour of mercuric oxide with trisodium imidosulphonate, p. 960). Ammonia gives a white precipitate; so also does ammonium chloride; in this case it is probably amidomercuric chloride. Mercuric oxide dissolves slightly in solution of the mercury sodium salt, rendering it alkaline. Both nitric acid and, still more so, hydrochloric acid dissolve the salt freely; apparently nitric acid does not immediately decompose it, but hydrochloric acid does completely. If the quantity of this acid is insufficient for the whole of the salt, its action is confined to its equivalent quantity, the rest of the salt being left undissolved, and no preferential replacement of the sodium or the mercury by hydrogen taking place. By extraction with ether, by evaporation, and by other tests, the change effected has been ascertained to be the formation of mercuric sodium chloride, sodium hydrogen sulphate, and amidosulphonic acid.

Analysis has given the following results:—

	$HgN_2(SO_3Na)_4,6H_2O$.	Found.	
Mercury....	26·74	27·16	
Sodium	12·30	12·35	
Sulphur....	17·11	17·19	
Nitrogen ...	3·74	3·95	
Water	14·44	13·15	8·86 lost *in vac.* 4·29 „ at 100°.

The exposure in the vacuum was for 40—45 hours; the further loss at 100° was the greatest obtainable in undried air, longer heating being followed very slowly by increase of weight. As analysed, the salt shows nearly a tenth less than the water calculated. Efflorescence of the sample was not noticed, but may have occurred to a slight extent. The main cause of the deficiency is, without doubt, fixation of some of the water of crystallisation or of atmospheric moisture by hydrolysis.

Oxymercuric Sodium Imidosulphonate.—In the preparation of this salt, the sodium imidosulphonate is taken in twice the molecular proportion to the mercuric nitrate; the result is satisfactory. The highly acid mother liquor retains much of the salt in solution, but it is thrown down if it is nearly neutralised with sodium hydroxide, and then contains scarcely any other mercuric or imidosulphonic salt. There is, however, no necessity to adhere closely to the calculated proportions, provided the sodium salt is neither in quantity great enough to redissolve the precipitate as mercuric disodium salt, nor so small as to leave the nitrate in great excess; it is, however, better to use too little than too much of the nitrate, especially if its solution contains any quantity of free acid.

Any precipitation of oxynitrate which water alone would cause in the solution of mercuric nitrate, is prevented by the presence of the sodium imidosulphonate, as this salt forms its basic mercury derivative by liberating half the nitric acid of the nitrate that it decomposes, and this acid is more than enough to keep any remaining nitrate from passing into oxynitrate; consequently, the washed precipitate is always free from nitrate. It may be washed sufficiently with water, which only very slightly acts on it, and may then be dried, either on paper or better on a tile.

On attempting to form a third and intermediate mercury sodium salt, which was to have the formula $O[HgN(SO_3Na)_2]_2$, analogous to the oxynitrate, $O(HgNO_3)_2$, we got, instead, only the two other salts, one in solution, the other as a precipitate. The oxymercuric sodium salt was thus obtained from a solution which, from first to last, was never acid, even the mother liquor being still faintly alkaline. The sulphonate and nitrate were used in the proportion

$$2NaN(SO_3Na)_2 : Hg(NO_3)_2;$$

the nitrate was added gradually, with stirring, to the dilute solution of the sulphonate, and simultaneously a solution of sodium hydroxide was run in, in the proportion of nearly five-sixths of a molecular quantity. In this way much yellow mercuric oxide was formed, along with the white precipitate, but by prolonged stirring, the precipitate lost all tinge of yellow. The mother liquor now contained much disodium mercury imidosulphonate, and the precipitate, washed and drained on a tile, proved to be pure oxymercuric sodium imidosulphonate (analysis *d*). Allowing for sodium hydroxide used in neutralising the free nitric acid present in the mercury nitrate solution, the reaction appears to be that expressed by the equation

$$6NaN(SO_3Na)_2 + 6Hg(NO_3)_2 + 4NaOH = 2HgN_2(SO_3Na)_4 \\ + Hg(OHgSO_3)_2NHgN(SO_3Na)_2 + 12NaNO_3 + 2H_2O.$$

Oxymercuric sodium imidosulphonate contains water of crystallisation, and appears to be slightly efflorescent; otherwise, it is permanent for a long time, whether wet or dry, though ultimately it decomposes and becomes yellowish-brown. Protracted washing with water decomposes it, as does also digestion with concentrated mercuric nitrate solution, a residue of the hydrogen oxymercuric salt being left in both cases (p. 978). It is very stable if but moderately heated, losing nearly the whole of its water of crystallisation.

At about 135° it permanently changes colour slightly, and at a much higher temperature melts to a dark, red-brown liquid and effervesces, decomposing in a way essentially the same as that of the normal mercury sodium salt. Even very gradual heating in a current of dried air, at a temperature of 170°, fails to expel more than four-fifths of the water, in consequence, no doubt, of hydrolysis.

It is much more readily dissolved by hydrochloric acid than by nitric or sulphuric acid. From its hydrochloric acid solution it cannot be recovered by neutralisation, being almost instantly decomposed, like the normal mercuric sodium salt. It is converted by sodium hydroxide into insoluble mercuric oxide, and mercuric disodium imidosulphonate, which remains dissolved. Its basic composition is at once demonstrated by the action on it of sodium chloride, which leaves insoluble mercuric oxide, and dissolves the rest, probably, as the two salts, mercuric sodium imidosulphonate and mercuric sodium chloride. Trisodium imidosulphonate dissolves it, but not to a large extent. If the solution of this salt is concentrated, a little mercuric oxide may separate, but the addition of water causes this gradually to dissolve. When, however, the trisodium salt is added to the oxymercuric sodium salt, still in its mother liquor, free dissolution at once occurs; but without the mother liquor, the reaction is as above stated.

The composition of the salt may be expressed, as shown by the following analytical results, by the formula $OHg_2N(SO_3)_2Na,(OH_2)_2$, which has, however, to be doubled to represent its constitution. The water comes out low, partly because of loss by efflorescence, but mainly by getting fixed through hydrolysis.

	Calculated.	(*a.*)	(*a.*)	(*b.*)	(*c.*)	(*d.*)
Mercury	61·63	62·18	61·22	61·56	—	61·73
Sodium	3·54	3·87	4·14	3·97	3·57	3·56
Sulphur	9·86	10·23	10·06	10·03	—	9·79
Nitrogen	2·16	—	2·27	2·24	—	—
Water	5·55	—	4·44	—	4·88	4·58

The preparation, *a*, was precipitated from 3 mols. of mercuric nitrate by 2 mols. of imidosulphonate, whilst *b* was got by adding sodium hydroxide to the decanted mother liquor of *a*. The preparation, *c*, was precipitated from 2 mols. of nitrate by 1 mol. of imidosulphonate, and *d* was formed with a non-acid mother liquor. All preparations, as well as their mother liquors, were free from sulphate.

The formation of oxymercuric sodium imidosulphonate is expressed by the equation

$$4Hg(NO_3)_2 + 2NaN(SO_3Na)_2 + 2H_2O = \\ Hg(OHgSO_3)_2NHgN(SO_3Na)_2 + 4NaNO_3 + 4HNO_3.$$

This reaction is noticeable for being one in which the sodium in the precipitate is not removed by the nitric acid; but, if imidosulphonic acid be regarded as a weaker acid than nitric acid, the precipitation of potassium nitrate by tartaric acid or perchloric acid is quite as remarkable, whilst if, as is most probable, it is like sulphuric acid, then the retention of the sodium is only natural. It is hardly noticeable for the precipitation of a basic salt with production of nitric acid, since similar reactions are common with oxygenous mercuric salts.

In its constitution, as regards the oxylic mercury, oxymercuric sodium imidosulphonate resembles oxymercuric sulphate and oxymercuric sulphite, as represented in the following formulæ (Trans., 1886, **49**, 553):—

Imidosulphonate.. $(NaO.SO_2)_2\!:\!N{\cdot}Hg{\cdot}N\!:\!(SO_2{\cdot}O{\cdot}Hg{\cdot}O)_2\!:\!Hg.$
Sulphate .... $Hg\!:\!(O{\cdot}Hg{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}Hg{\cdot}O)_2\!:\!Hg.$
Sulphite .... $Hg\!:\!(SO_2{\cdot}O{\cdot}Hg{\cdot}O)_2\!:\!Hg.$

Constitution of the Mercury Imidosulphonates.

From the widely established character of the relation between mercury and the nitrogen of ammonia and cyanogen, and from that of the mercury in its oxygenous salts, particularly those of sulphuryl, such as sulphites and sulphates, the relations of mercury in its imidosulphonates become of much interest, as likely to differ from those of other basylous elements.

Firstly, as to the mercury disodium and mercury dipotassium imidosulphonates, no hesitation will be felt in accepting for these salts—say that of sodium—the formula $HgN_2(SO_3Na)_4$ (Berglund). Yet this point is not so simple as it seems. Calcium forms the salt, $CaNaN(SO_3)_2$; silver forms the salt, $Ag_2NaN(SO_3)_2$; and mercury itself, the salts, $OHg_2NaN(SO_3)_2$ and $O_2Hg_3HN(SO_3)_2$. All these salts have only one-third of the bases either as sodium or hydrogen, and it will be well, therefore, to briefly review the reasons for writing $HgN_2(SO_3Na)_4$.

Disodium hydrogen imidosulphonate is a salt neutral, or only slightly acid to, litmus, although active as an acid, and, therefore, it cannot contain the group, SO_3H, since this always gives to its compounds acidity and a strong action on blue litmus. It must, therefore, be written $HN(SO_3Na)_2$. Mercury readily takes the place of the hydrogen of this salt, or of 1 atom of the sodium of the alkaline trisodium imidosulphonate, and the resulting mercury disodium salt is neutral in reaction. Transposition of the metals cannot be admitted to take place in its formation for two reasons. One is, that the alkaline reaction of the trisodium salt disappears when it becomes the mercury sodium salt, and there is no accounting for this if the mercury displaces the sulphonic sodium. The other reason is, that if the mercury takes the sulphonic relation in the salt, this salt would be an exception to the observation that all the oxylic mercuric salts capable of existing in presence of water are insoluble basic or oxysalts.

This theory of the constitution of the normal mercury double sulphonates accords with the interesting behaviour of these salts towards acids and alkalis. The latter only partially precipitate mercuric oxide from them, because the mercury is in immediate relation with (unoxidised) nitrogen. Nitric acid, which can replace the mercury by hydrogen, cannot do the same with the potassium or sodium, because this is in oxylic relation to sulphuryl, as it is in sulphates, and is, therefore, irremovable by this acid. Sulphuric acid also first replaces the mercury by hydrogen, when acting on the mercury potassium salt, although from the mercury barium salt it first takes the barium away.

Berglund would have chemists regard mercury imidosulphonates as salts of an independent acid, in which mercury is combined with special force. A fuller knowledge of the imidosulphonates does not tend to support this view. There are other series of double imidosulphonates besides that of mercury, apparently the only one observed by him; normal mercury hydrogen imidosulphonate has even less stability than imidosulphonic acid itself; oxymercuric hydrogen imidosulphonate is far more stable; dipotassium and disodium hydrogen imidosulphonates have equal or greater claims to be treated as particular acids; lastly, it is highly probable that, powerfully as mercury takes the place of hydrogen in ammonia itself, it will have little of that power when two-thirds of that hydrogen have already been replaced by sulphonic radicles.

The constitution of the salt in which two-thirds of the base of the trisodium salt are replaced by mercury next requires attention. It might be treated as having the single atom of sodium in the odd basylous position, that is, united to the nitrogen; but against this four objections present themselves. One is that it is highly improbable that the sodium should hold the imidic relation rather than the sulphonic. A second is that it is quite as unlikely that a mercury atom should be united half to nitrogen and half to oxygen, whilst it is usual to find it thus united at once to oxygen and to an oxygenous radicle. A third objection is, that whereas in other cases sulphuryl takes $1\frac{1}{2}$ atoms of mercuric oxide to saturate either of its valencies, it does not do so in this salt unless the sodium is given to one of the sulphuryls of the salt. The fourth objection lies in the great improbability that sodium in the imidic relation would resist, as it here does, displacement by hydrogen on treating the salt with nitric acid. Avoiding these four difficulties by placing one-fourth of the mercury with the nitrogen, there remains the usual $1\frac{1}{2}$ atoms to unite with half one of the sulphuryls. The relations of the salt, and its constitution as here developed, require that its formula should be double that expressed in the lowest terms, in order to allow of the oxylic mercury being shown apart from the non-oxylic

$$Hg\dot{:}(O{\cdot}Hg{\cdot}O{\cdot}SO_2)_2\dot{:}N{\cdot}Hg{\cdot}N(SO_3Na)_2.$$

It now becomes clear that the sodium resists the action of nitric acid, because it is in oxylic relation to sulphuryl, as pointed out in discussing the constitution of the normal mercury disodium salt; that nitric acid removes a fourth of the mercury, replacing it by hydrogen, because this fourth part is in relation to the nitrogen; that nitric acid does not remove the rest of the mercury, because this exists as the oxymercuric group found in sulphate and sulphite, in oxylic relation to sulphuryl, also resisting the action of nitric acid; and, lastly, it becomes clear how it is that the oxymercuric hydrogen imodosulphonate has quite consistently a constitution different from that of the oxymercuric sodium salt, and how the one salt is formed from the other (compare Divers and Shimidzu, "On Mercury Sulphites," Trans., 1886, **49**, 574).

In fact, the constitution of the oxymercuric hydrogen imidosulphonate follows obviously from the production of the salt by (acid) mercury nitrate in excess. From what we actually can observe in the case of the normal mercury dipotassium salt, we know that nitric acid of itself should act as represented by this equation:—

$$\begin{aligned}&Hg(OHg{\cdot}O{\cdot}SO_2)_2NHgN(S_3ONa)_2 + 2HNO_3 = \\ &\qquad Hg(OHg{\cdot}O{\cdot}SO_2)_2NH + HN(SO_3Na)_2 + Hg(NO_3)_2,\end{aligned}$$

replacing the imidic mercury by hydrogen, but not touching the oxymercuric group in conformity with its inability in other cases (sulphites and sulphates) to do so when the group is joined to sulphuryl. In the absence of mercuric nitrate, this reaction is slowly followed by hydrolysis of the disodium hydrogen salt through the unadvoidable excess of nitric acid, but in presence of mercuric nitrate hydrolysis does not take place. The mercuric nitrate finishes the formation, just formulated, of the oxymercuric hydrogen salt, in the way shown by the equation

$$HN(SO_3Na)_2 + 3Hg(NO_3)_2 + 2H_2O = HN(SO_2{\cdot}O{\cdot}HgO)_2Hg + 2NaNO_3 + 4HNO_3,$$

from which equation it will also be sufficiently clear how the whole change can be effected by mercuric nitrate without any addition of nitric acid.

From the constitution given to this salt, it is at once evident why it can be left for days in a nitric acid solution of mercuric nitrate without becoming hydrolysed; for hydrolysis can only occur when some of the sulphonic group becomes acid, or SO_3H, and here the nitric acid, especially in presence of much mercuric nitrate, is powerless to displace the oxymercuric group by hydrogen.

There remains now only to tabulate the three mercuric salts, the constitution of which has been discussed, in order to bring out their relations quite clearly, and particularly the intermediate relation of the oxymercuric sodium salt:—

Imidosulphonate.	Formula.
Mercuric disodium	$Hg{<}\begin{matrix}N(SO_3Na)_2\\N(SO_3Na)_2\end{matrix}$.
Oxymercuric sodium....	$Hg{<}\begin{matrix}N(SO_3Na)_2\\N(SO_3{\cdot}Hg{\cdot}O)_2Hg\end{matrix}$.
Oxymercuric hydrogen..	$HN(SO_3{\cdot}Hg{\cdot}O)_2Hg$.

ADDENDUM.

Oxyamidosulphonates.—In our last paper sent to the Society, which appeared in the Journal so far back as 1889, we had to call attention to the discrepancy between some of the results of the work on *sulphazotised salts* done by others and by ourselves. We are glad to be able now to bring in support of the accuracy of certain of our own statements, the testimony of Dr. Raschig, who wrote, soon after the appearance of the paper on *oxyamidosulphonates*, to request us, when next publishing, to make known that he now entirely agrees with our account of the decomposition of oxyamidosulphonates by caustic alkali (Trans., 1889, **55**, 765), and withdraws his own statement concerning it, which was based upon qualitative reactions only.

LXXXIII.—*Modification of Beckmann's Boiling Point Method of Determining Molecular Weights of Substances in Solution.*

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Recent investigations in Physical Chemistry have greatly extended our means of determining the molecular weights of substances. Besides the ordinary method which depends on the determination of the relative density of a substance in the gaseous state—the so-called "vapour density" method—we have now, thanks to the labours of Raoult and others, various means of ascertaining molecular weights of substances in solution. Diminution of vapour tension, lowering of the freezing point or rise of the boiling point of a solvent, are the changes which accompany the dissolution of a solid in it, and each of these changes supplies us with a means of determining the molecular weight of the dissolved substance. These are mutually connected together by theoretical considerations, but for purposes of determining molecular weights, the method depending on the change in the boiling point far surpasses the others, both on account of the simplicity of the manipulation and of the greater accuracy in the results obtained. We are indebted to Beckmann (*Zeit. physikal. Chem.*, **3**, 603 [1889]; **4**, 532 [1889]; **5**, 76 [1890]; **6**, 437 [1890]; **8**, 223 [1891]) for this method; but, in spite of his indefatigable labours, there are some points in the practical carrying out of his method, which are capable of improvement and simplification. The object of the present paper is to describe a modification, which renders it available in every laboratory, and, at the same time, capable of yielding results which are even more concordant than those obtained by Beckmann himself.

It may, however, not be out of place to first briefly refer to the principle which underlies this method. From a study of the lowering of vapour pressure of various solvents produced by the substances dissolved in them, Raoult was ultimately led to formulate the law that "The relative lowering of vapour pressure is proportional to the ratio of the number of molecules of the dissolved substance to the total number of molecules in the solution." Or expressed in a formula—

$$\frac{p - p'}{p} = c \times \frac{n}{\mathrm{N} + n},$$

where p and p' are the vapour pressures of the solvent and of the solution, and N and n, the number of molecules of the solvent and of the dissolved substance respectively. The constant c may be taken as equal to unity. If, then, G and g be the weights taken, and M and m the molecular weights, of the solvent and of the dissolved substance, all expressed in grams, we have—

$$\frac{p - p'}{p} = \frac{\frac{g}{m}}{\frac{G}{M} + \frac{g}{m}},$$

$$\text{or } m = M \cdot \frac{g}{G} \cdot \frac{p'}{p - p'}.$$

Hence, if M, G, and g are known, the molecular weight of the dissolved substance, m, is given by determining p and p', the vapour pressures of the solvent and of the solution.

Now, the diminution of vapour pressure is proportional, on the one hand, to the lowering of the freezing point and, on the other, to the rise of the boiling point. The former relation, which was established by Raoult in a purely empirical way (*Compt. rend.*, **87** [1878]; **103** [1886]; **104** [1887]; **105** [1887]; **107** [1888]; (*Ann. Chim. Phys.* [6], **15** [1888]), had already been deduced by Guldberg (*Compt. rend.*, **70** [1870]) from the mechanical theory of heat. Moreover, Van't Hoff (*Zeit. physikal. Chem.*, 1887, **1**, 494) theoretically deduced the laws of the lowering of the freezing points of solutions from the relation which exists between vapour pressure and osmotic pressure.

The determination of the other relation, the rise of the boiling point, also affords us a means of ascertaining the molecular weight of the dissolved substance, inasmuch as it is possible to determine the temperatures at which the solvent and the solution exhibit equal vapour pressures, instead of ascertaining their vapour pressures at the same temperature. This method was first practically carried out by Beckmann (*loc. cit.*).

The calculation of the molecular weight is made by taking into consideration the proportionality which exists between the difference of pressure and the difference of temperature. Now, since the solutions subjected to examinations are all very dilute, the equation

$$\frac{p - p'}{p} = \frac{n}{N + n}$$

may assume the following form without causing any material difference in the results:—

$$\frac{p - p'}{p} = \frac{n}{N}.$$

The difference of temperature produced in the boiling point by the dissolution of the substance in the proportion of 1 gram-molecule to

1 gram-molecule of the solvent, and which corresponds to the above pressure-difference, is called the *molecular elevation of boiling point.*

This constant is obtained experimentally by determining the rise of boiling point of a solvent, following the dissolution of a known weight of a substance of known molecular weight in a known quantity of the solvent. Thus, for example, Beckmann (*Zeit. physikal. Chem.*, 1889, **3**, 603), found that 4·740 grams of ethyl benzoate dissolved in 100 grams of ether raised the boiling point of the latter by 0·665°. The weight of ethyl benzoate dissolved in 1 gram-molecule of ether (74 grams) is, therefore, $\frac{4{\cdot}740 \times 74}{100} = 3{\cdot}5076$ grams. The rise of boiling point corresponding to the dissolution of 1 gram-molecule of ethyl benzoate (150 grams) in 1 gram-molecule of ether would then be—

$$\frac{0{\cdot}665 \times 150}{3{\cdot}5076} = 28{\cdot}4.$$

Experiments with other substances give nearly the same value for the molecular elevation of the boiling point of ether. The molecular weight of any dissolved substance is then obtained from the equation

$$m = \mathrm{B} \times g/\Delta,$$

where, in the case of ether, $\mathrm{B} = 28{\cdot}4$, g = weight of the substance dissolved in 74 grams of ether, and Δ = the observed rise of boiling point.

In practice, it is more convenient to refer the constant B to 100 grams, instead of to the molecular weight, of the solvent; the calculation is thus very much simplified. The formula then becomes—

$$m = \mathrm{B}' \times g'/\Delta,$$

where, in case of ether, $\mathrm{B}' = 28{\cdot}4 \times 74/100 = 21{\cdot}0$, and g' = weight of the substance dissolved in 100 grams of the solvent. As the mean of several determinations, Beckmann (*loc. cit.*) obtained the number 20·9 for the value of B′.

The constant B or B′ may, moreover, be accurately calculated in the following manner from the latent heat of vaporisation and the boiling point of the solvent, as has been pointed out by Arrhenius (*Zeit. physikal. Chem.*, 1889, **4**, 550).

Suppose we have a solvent of molecular weight M, and of boiling point T (in absolute temperature) at pressure p. By dissolution of n gram-molecules in 100 grams of the solvent, the boiling point rises to $\mathrm{T} + d\mathrm{T}$. The relation between this rise, $d\mathrm{T}$, and the dissolved mass, n, may be calculated thus:—

The solution boils under pressure p at the temperature $T + dT$. The vapour pressure of the solvent at T is equal to p; it is equal to $p + dp$ at the temperature $T + dT$. Between dT and dp the following relation exists, according to the second law of thermodynamics, as already shown by Van't Hoff (*Zeit. physikal. Chem.*, 1887, **1**, 494):—

$$\frac{dp}{p} = dT \cdot \frac{w}{2T^2},$$

where w = latent heat of vaporisation of a gram-molecule of the solvent at temperature T.

Now, according to Raoult's law, the relation between the diminution of vapour pressure and the number of molecules of the solvent and of the dissolved substance is expressed by—

$$\frac{p - p'}{p} = \frac{n}{N + n},$$

$$\text{or } \frac{(p + dp) - p}{p + dp} = \frac{n}{N + n},$$

$$\text{or } \frac{dp}{p + dp} = \frac{n}{N + n}.$$

But, as the solution is very dilute, dp is very small compared to p, and n very small compared to N. The last equation may, therefore, be written as

$$dp/p = n/N,$$

or, as 100 grams of the solvent is employed and M = its molecular weight, we have—

$$dp/p = n \, . \, M/100.$$

Equating this value of dp/p with that already obtained, we have—

$$\frac{n \, . \, M}{100} = \frac{w \, . \, dT}{2T^2}.$$

In this equation, w being the latent heat of vaporisation of a gram-molecule of the solvent (M grams) in gram-calories, it follows that w/M = latent heat of vaporisation of 1 gram of the solvent. Calling this W, we have—

$$\frac{n \, . \, M}{100} = \frac{M \, . \, W \, . \, dT}{2T^2},$$

$$\text{or } dT = n \times 0{\cdot}02T^2/W.$$

If s = weight of the substance dissolved in 100 grams of the solvent, and m = molecular weight of the dissolved substance, then

$n = s/m$. Substituting this value of n in the above equation, and solving for m, we have—

$$m = \frac{0{\cdot}02\mathrm{T}^2}{\mathrm{W}} \cdot \frac{s}{d\mathrm{T}}.$$

In this equation, s and dT have the same meaning as g' and Δ respectively in one of the preceding operations (p. 991); and the constant, $0{\cdot}02\mathrm{T}^2/\mathrm{W}$, for ether is found to be equal to

$$\frac{0{\cdot}02 \times (273 + 34{\cdot}97)^2}{90{\cdot}1} = 21{\cdot}0,$$

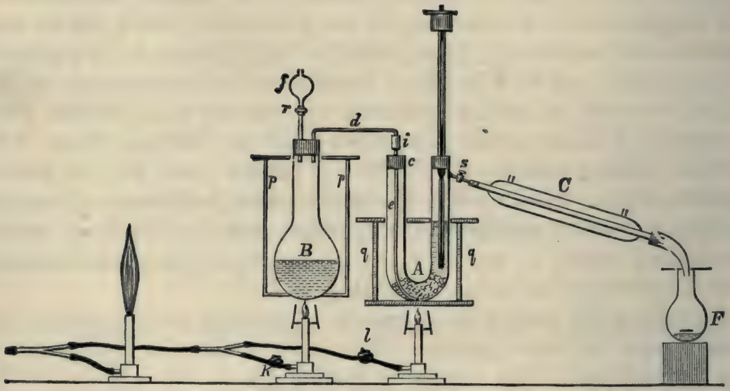
the value which we already obtained for B′ in the same equation.

Now, turning to the practical side of the question, the great and the only difficulty which lies in the way is the exact determination of the boiling points, as has already been pointed out by Beckmann. Irregular boiling and bumping, attended with sudden alterations in the temperature of a boiling liquid, are phenomena which are too well known to be mentioned. Even when the liquid seems to be regularly boiling, there are still constant changes in the temperature of the liquid, as may be readily observed by the use of a delicate thermometer. Various means have been tried to overcome these difficulties. Bits of metallic wire or foil, of broken glass, &c., are almost useless. Raoult tried coating the thermometer bulb with a layer of palladium recently charged with hydrogen gas, but it did not lead to the desired result, as the evolution of hydrogen gas soon slackened, and in about 20 minutes stopped altogether.

Beckmann has succeeded in greatly overcoming the difficulties. He uses a piece of stout platinum wire which is fixed in the bottom of the boiling vessel by means of fusible glass. On account of the superior thermal conductivity of the metal, the boiling is said to take place exclusively from the piece of platinum, and bumping is avoided entirely. I regret to say that I have not yet had any experience in the use of Beckmann's apparatus. In fact, we ordered one from Germany, but on my first attempt to make trial of it, the boiling vessel was found to be cracked at the point of insertion of the platinum. This was merely an accident, but it is an accident which may not unfrequently occur. A small portion of the bottom of the boiling vessel is thickened by the fusible glass, and it is not surprising that the bottom should be cracked by the slightest carelessness in heating.

The means which I adopt in producing a constant temperature in the boiling liquid has already been described in my paper on "The Determination of the Temperature of Steam arising from Boiling Salt Solutions" (this vol., p. 495), and consists in passing a current of the vapour of the solvent into the boiling liquid or solution, the amount of the vapour thus passed in from without being regulated by the height of the lamp. The degree of constancy of the temperature attained in this manner by the boiling liquid is really astonishing, a most delicate thermometer, capable of showing 1/1000th of a degree, remaining almost stationary.

Description of Apparatus.—Instead of the three-necked flask with a piece of platinum wire fixed into the bottom, and with a complex condensing arrangement, used by Beckmann, I employ for the *boiling vessel* an ordinary U-tube A, about 2 cm. in internal diameter, and 21 cm. in height. Near the top of one of the limbs of this U-tube a hole is blown out by means of the blowpipe, which serves for joining on, with a piece of india-rubber tubing, a small side tube, having a glass stop-cock *s*. The side-tube is, in its turn, connected with an ordinary Liebig's condenser C. The *boiler* for generating the vapour of the solvent is an ordinary round-bottomed flask B, provided with a cork, through which pass the stem of a tap-funnel, *f*, and a delivery tube, *d*. The latter is connected, by means of a piece of thick india-rubber tubing, *i*, with a tube, *e*, drawn out and slightly bent at its lower end, so that this end of the tube may just reach the bottom of the boiling vessel when the cork, through which it passes above, is fixed into the mouth of the U-tube, nearest to the boiler. This tube *e* thus establishes communication between the boiler and the boiling vessel. A tin-plate vessel, *pp*, with a hole in the bottom, and resting upon a tripod, serves to enclose the boiler, and to protect it from draughts. The boiling vessel is, on the other hand, enclosed by a box made of thick asbestos cardboard, *qq*, with a movable bottom. When the solvent is of low boiling point, such as carbon bisulphide or ether, a piece of plain asbestos cardboard serves as the



bottom of the box, and the boiling vessel is heated by indirect flame, as shown in the figure. In the case, however, of less volatile solvents, such as water, or even alcohol, a piece of asbestos cardboard, having a hole in the centre, is used instead, and the boiling is effected by the direct application of a flame.

The height of the flame both under the boiler and the boiling vessel has to be carefully regulated for each particular solvent according to its volatility; and, in order to avoid the effect of any alteration in the gas pressure, owing to constant openings and shuttings of gas taps in other parts of the laboratory, the following arrangement is adopted and is found to answer admirably. The gas tube is connected with three Bunsen burners and, fully opening the gas tap, the burner nearest the tap is lighted. This acts as a gas regulator. The supply of gas to the other two burners is adjusted by means of screw-clips *k* and *l*; and, since the amount of gas supplied to the regulator burner is incomparatively greater than that supplied to the two others, no effect of alterations of gas pressure in the mains can be perceived in the latter. This circumstance is of considerable importance, because I am thereby enabled to use the bulb of the thermometer always naked, there being no necessity to envelop it with asbestos fibres, as when working with Beckmann's apparatus.

The thermometer which I use includes only a range of 6° C., and is graduated into 1/100ths of a degree. Each of these divisions (about 0·4 mm.) can be readily estimated to 1/10th by means of a reading telescope, which I always use, so that the thermometer can indicate 1/1000 of a degree. There is an arrangement in the instrument by which the quantity of mercury in the bulb may be increased or diminished, so that it can be used either for low or high temperatures. This instrument has already been described by Beckmann.

The whole arrangement is exceedingly simple, and can be set up by any one with materials commonly found in all laboratories. This, I venture to say, is a great advantage. The only costly part of the apparatus is the thermometer, but for good and accurate work in most physico-chemical inquiries, a delicate thermometer is indispensable and, after all, its cost is not disproportionate to the important services it can render.

Mode of Working.—For working with the apparatus described above, I begin by inserting the tube *e* into one limb of the boiling vessel, fixing it by means of the cork *c*. Small glass beads are then introduced into the boiling vessel through the other limb, till they quite fill the bent portion of the latter. (Beckmann recommends the use of small garnets or glass beads for preventing local differences of temperature, and I find them also very effective for thoroughly mixing the vapour passed in with the boiling liquid and thus establishing a perfect uniformity of temperature.) The experimental liquid is now poured in, so that it occupies a space of three or four centimetres above the level of the glass beads in the open limb, and the latter is then closed by the cork carrying the thermometer. The lid of the asbestos box is next slipped down the two limbs of the tube, which pass through two holes previously made in it in proper positions, and the boiling vessel, after having been properly enclosed in the asbestos box and supported on the ring of a retort-stand, is connected, on the one side, with the boiler and, on the other, with the side-tube and condenser, as shown in the figure.

First the boiler, half filled with the solvent, and then the boiling vessel are heated by carefully regulated lamps, the stop-cocks *r* and *s* both open; and, when the liquid in both vessels begins to boil properly, the stop-cock *r* is closed, and the two lamps very carefully regulated, so that the height of the column of the boiling liquid remains, as nearly as can be judged, level with the lid of the asbestos box for, at least, a quarter of an hour. This circumstance is used as the criterion that the boiler and the boiling vessel are each being heated by a properly adjusted lamp, so that evaporation and condensation balance each other in the boiling vessel. The thermometer rises rapidly at first, but more slowly afterwards, attains the maximum temperature in 10 or 12 minutes, and then remains perfectly constant. The top of the thermometer is now lightly tapped for some seconds, and the observation of the exact temperature made by the aid of a reading telescope. Finally, the volume of the distillate collected in the small flask F is noted and, after withdrawing the lamps, the stop-cock *r* is opened and the stop-cock *s* closed.

I make it a rule to repeat this observation of the exact boiling point of the solvent once or, in some cases, twice more in order to make sure of the temperature. For this purpose, the distillate is returned to the boiler and the whole of the above process repeated under exactly the same conditions as before, taking the final observation of the temperature when the distillate reaches the mark previously made on the receiver flask.

The next step is to introduce the substance into the solvent. This may be done in two ways. The first and simplest method, which should be used when the solvent is of low boiling point, consists in taking out the cork which carries the thermometer, adding the solid substance to the solvent, and then immediately replacing the cork in its original position. The other method, which is employed in the case of solvents of high boiling point, and where, therefore, if the first method were adopted, the highly heated thermometer would have to be suddenly exposed to the cold air, is as follows: After the exact determination of the boiling point of the solvent has been made, the boiler is a little cooled without opening the stop-cock *r*, when a small quantity of the solvent runs up the tube *e* and flows down into the boiler. The stop-cock *r* is now opened and then, disconnecting the delivery tube *d* from the tube *e*, a small quantity of a concentrated solution of the substance, made beforehand, is introduced into the boiling vessel by means of a small funnel attached to the india-rubber tubing *i*. After removing the funnel, communication is re-established between the boiler and the boiling vessel.

The lamps, which have been put aside but not turned out, are next brought under the two vessels as before, and the boiling point of the solution determined in exactly the same manner and under exactly the same conditions as those in which the boiling point of the solvent was determined, collecting, of course, the same quantity of the distillate. When the exact temperature has been ascertained, the lamps are put out, the stop-cock *r* opened, the stop-cock *s* closed, and the whole apparatus allowed to cool.

After the solution has completely cooled, the percentage composition is determined, by transferring some of the solution to a weighed, stoppered bottle by means of a pipette, and, after ascertaining the weight of the solution taken, evaporating it at a gentle heat on a water-bath, and weighing the fixed residue. In the case of iodine, it is determined volumetrically by a standard solution of sodium thiosulphate.

From the account of the process above given, it will be seen that it differs from that used by Beckmann essentially in that, whilst Beckmann takes a weighed quantity, both of the solvent and of the solid substance, and determines the boiling points in an apparatus provided with a reflux condenser, and, therefore, requires a complicated arrangement, the method here described requires no special apparatus, as it determines the boiling points in the ordinary manner, but obviates the usual difficulties of such determinations, and, at the same time, keeps the quantity of the boiling liquid constant, by passing in a current of the vapour of the solvent from without. Another difference, which, I venture to say, is also an improvement, is that the boiling point of the solution is ascertained just before its composition is determined, and the connection between these properties is, therefore, rendered more certain than in the case of Beckmann's method. The results of my determinations are contained in the following tables (pp. 998—1001).

In conclusion, a word may be said with regard to the molecular weights of iodine and of sulphur in solution. Paternò and Nasini (*Ber.*, 1888, **21**, 2153), by the depression of the freezing point, found that the molecular weight of iodine in very dilute benzene solutions

Solvent: *Water.*

Lat. Ht. Vap. = 536·4 (Regnault, 1847); b.p. = 100° C. $\frac{0{\cdot}02T^2}{W} = 5{\cdot}2$.

Substance.	B. p.			Grams of solution.	Grams of substance.	Grams of solvent.	Grams substance per 100 grams solvent.	Observed molecular weight.	Diff. per 100.
	Solvent.	Solution.	Rise.						
Mercuric chloride, $HgCl_2$ = 271	2·262	2·441	0·179	10·6755	0·8795	9·7960	8·978	**260·8**	−3·8
,, ...	2·305	2·389	0·084	10·4385	0·4258	10·0127	4·253	**263·3**	−2·8
Mannite, $C_6H_8(OH)_6$ = 182..........	2·214	2·406	0·192	11·2302	0·6855	10·5447	6·501	**176·1**	−3·2
,, ...	2·265	2·396	0·131	11·7120	0·5196	11·1924	4·642	**184·1**	+1·2
,, ...	2·403	2·483	0·080	9·5396	0·2637	9·2759	2·843	**184·8**	+1·5
Cane Sugar, $C_{12}H_{22}O_{11}$ = 342.........	2·475	2·680	0·205	10·7289	1·2980	9·4309	13·775	**349·4**	+2·2
,, ...	2·317	2·447	0·130	11·7419	0·9175	10·8244	8·476	**339·0**	−0·9
,, ...	2·649	2·713	0·064	10·6146	0·4392	10·1751	4·316	**350·7**	+2·5
,, ...	2·653	2·688	0·035	10·7965	0·2579	10·5386	2·447	**363·5**	+6·3

Solvent: *Ethyl Alcohol.*[*]

Lat. Ht. Vap. = 214·9 (Regnault, 1862); b.p. = 78°·3 C. $\frac{0{\cdot}02T^2}{W} = 11{\cdot}5.$

Substance.	B. p.			Grams of solution.	Grams of substance.	Grams of solvent.	Grams substance per 100 grams solvent.	Observed molecular weight.	Diff. per 100.
	Solvent.	Solution.	Rise.						
Acetanilide, $C_6H_5{\cdot}NH{\cdot}C_2H_3O$ = 135...	3·720	4·191	0·471	8·0628	0·4338	7·6290	5·686	**138·8**	+2·8
" ..	3·554	3·705	0·151	8·3318	0·1410	8·1908	1·721	**131·1**	−2·9
" ..	3·793	3·906	0·113	8·2361	0·1090	8·1271	1·341	**136·5**	+1·1
" ..	3·581	3·667	0·086	8·0012	0·0817	7·9195	1·032	**138·0**	+2·2
Salicylic acid, $OH{\cdot}C_6H_4{\cdot}COOH$ = 138.	3·984	4·515	0·531	8·0762	0·4772	7·5990	6·280	**136·0**	−1·5
" ..	3·775	4·092	0·317	7·0653	0·2523	6·8130	3·704	**134·4**	−2·6
" ..	4·240	4·367	0·127	8·3855	0·1279	8·2576	1·549	**140·3**	+1·7
Mercuric chloride, $HgCl_2$ = 271......	4·050	4·521	0·471	6·8492	0·6717	6·1775	10·873	**265·5**	−2·0
"	3·731	4·111	0·380	8·2052	0·6612	7·5440	8·765	**265·2**	−2·1
"	3·702	3·848	0·146	8·4119	0·2774	8·1345	3·413	**268·9**	−0·8

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[*] Rendered anhydrous by distillation, first from freshly ignited lime and then from a small quantity of sodium.

Solvent: *Ethyl Ether.**

Lat. Ht. Vap. = 90·1 (Regnault, 1862); b.p. = 34°·9 C. $\frac{0{\cdot}02T^2}{W} = 21{\cdot}0$.

Substance.	B. p.			Grams of solution.	Grams of substance.	Grams of solvent.	Grams substance per 100 grams solvent.	Observed molecular weight.	Diff. per 100.
	Solvent.	Solution.	Rise.						
Salicylic acid, $OH{\cdot}C_6H_4{\cdot}COOH$ = 138 .	1·013	1·397	0·384	6·9880	0·1733	6·8147	2·543	**139·1**	+0·8
,, ..	1·337	1·661	0·324	7·2700	0·1591	7·1109	2·237	**145·0**	+5·1
,, ..	0·986	1·236	0·250	7·1384	0·1174	7·0210	1·672	**140·4**	+1·7
Naphthalene, $C_{10}H_8$ = 128	0·739	1·464	0·725	7·2743	0·3128	6·9615	4·493	**130·1**	+1·7
,, ...	1·038	1·541	0·503	7·0014	0·2143	6·7871	3·159	**131·9**	+3·0
,, ...	1·275	1·542	0·267	7·0232	0·1112	6·9120	1·609	**126·6**	−1·1
Iodine, I_2 = 254.....................	1·295	1·615	0·320	7·1600	0·2678	6·8922	3·886	**255·0**	+0·4
,, ...	1·098	1·302	0·204	7·2838	0·1796	7·1042	2·528	**260·2**	+2·4
,, ...	1·174	1·255	0·081	6·9250	0·0692	6·8558	1·009	**261·6**	+3·0

Redistilled over sodium.

Solvent: *Carbon Bisulphide.**

Lat. Ht. Vap. = 84·8 (Regnault, 1862); b.p. = 46°·2 C. $\frac{0\cdot02T^2}{W} = 24\cdot0$.

Substance.	B. p.			Grams of solution.	Grams of substance.	Grams of solvent.	Grams substance per 100 grams solvent.	Observed molecular weight.	Diff. per 100.
	Solvent.	Solution	Rise.						
Naphthalene, $C_{10}H_8$ = 128	3·480	3·860	0·380	7·6888	0·1433	7·5455	1·901	**120·0**	−6·2
"	3·385	3·718	0·333	12·4832	0·2192	12·2640	1·795	**130·5**	+1·9
Iodine, I_2 = 254	3·887	4·284	0·397	11·3537	0·4714	10·8823	4·332	**261·9**	+3·1
"	3·680	3·905	0·225	11·4810	0·2600	11·2210	2·317	**247·1**	−2·7
"	3·709	3·892	0·183	7·9370	0·1534	7·7836	1·971	**258·5**	+1·8
Sulphur, S_8 = 256	3·551	4·141	0·590	10·5998	0·6247	7·9751	6·263	**254·8**	−0·4
"	3·430	3·791	0·361	12·2753	0·4488	11·8265	3·795	**252·3**	−1·7
"	3·682	3·870	0·188	10·2030	0·1998	10·0032	1·997	**254·9**	−0·4

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* Purified by shaking with mercury and then distilling from dry litharge.

is represented by I_2, whilst it possesses higher values in more concentrated solutions. They found also that iodine is more or less dissociated into the atomic state in its solution in glacial acetic acid. Loeb (*Zeit. physikal. Chem.*, 1888, **2**, 606), however, could not verify these conclusions by the same method, and, both on account of the small solubility of iodine in either benzene or glacial acetic acid, and of the great variations in the results according to concentration, he ultimately gave up these experiments. By determining the vapour pressures of solutions of iodine in ether and in carbon bisulphide, Loeb showed, on the other hand, that the molecular magnitude of iodine in brown ethereal solutions is represented by I_4, whilst in carbon bisulphide it is less complex, and corresponds to the formula $I_{2\cdot4}$. Lastly, Beckmann (*ibid.*, 1890, **5**, 76) found, by the aid of his boiling method, that no appreciable difference exists in the molecular magnitude of iodine, whether dissolved in ether or in carbon bisulphide, and that it corresponds to I_2 in both of the solutions. The numbers he obtained varied between 235 and 256 in ethereal solutions, and between 250 and 272 in carbon bisulphide solutions ($I_2 = 254$). More recently, Hertz (*ibid.*, 1890, **6**, 358), by the freezing method, obtained numbers varying between 255·5 and 276 for the molecular weight of iodine in its dark red solution in naphthalene, and pointed out that the red colour of the iodine solution is not due to the existence of complex molecules, as already shown by Beckmann. My own determinations also fully confirm the results obtained by the latter.

With regard to the molecular weight of sulphur in carbon bisulphide solution, Beckmann, by the boiling method, obtained numbers varying between 245 and 281, and, therefore, pointing to the existence of complex sulphur molecules represented by $S_8 = 256$. The formula S_6 had generally been regarded as the maximum molecular formula of sulphur, and the results obtained by Beckmann, therefore, needed confirmation. The experiments by Hertz, who obtained numbers varying between 262·3 and 279·4 (*loc. cit.*), and, still more conclusively, my own determinations, put Beckmann's views beyond any doubt.

LXXXIV.—*Anhydro-derivatives of Citric and Aconitic Acids.*

By T. H. Easterfield and W. J. Sell.

Introduction.

Pilz (*Jahresbericht*, 1861, 368), Perkin (*Annalen*, Suppl., **5**, 287), and Anschütz (*Ber.*, **14**, 2791) have shown that by the long continued action of acetyl chloride on certain hydroxy bibasic acids of the aliphatic series acetyl anhydrides may be obtained. These derivatives have been but little investigated, though it can scarcely be doubted that they are likely to afford interesting derivatives. Bearing in mind the ease with which the ethereal salts of citric acid are converted into pyridine derivatives, it appeared of interest to attempt the preparation of an acetyl anhydro-citric acid by the above method; it was found that it could be readily obtained in almost quantitative yield, and our expectations as to its chemical activity were completely realised. Thus it combines with water to form acetylcitric acid, and by its action on ammonia forms citrazinic acid, whilst with aniline it yields citrodianilic acid. Boiling alcoholic potash eliminates acetic acid, and a very satisfactory yield of aconitic acid is obtained. If the anhydride is distilled, it loses carbon dioxide and acetic acid, and, according as the distillation is performed, under ordinary pressure or in a vacuum, citraconic or itaconic anhydride is produced.

The preparation of the hitherto undescribed anhydride of aconitic acid was undertaken as an almost necessary supplement to the above work. Full details of the experimental work appear in the following pages.

Acetanhydrocitric Acid.

If anhydrous citric acid is digested upon the water-bath for a couple of hours with a slight excess of acetyl chloride (calculated for 4 mols.), in a flask provided with a reflux condenser, complete dissolution takes place, and the contents of the flask, on cooling, set to a mass of crystals. If these are drained by the aid of the filter-pump, washed with a small quantity of acetyl chloride, and dried in a vacuum over sulphuric acid and solid potash, a snow-white substance is obtained. On analysis it gave numbers which agree with the formula $C_8H_8O_7$.

I. 0·1692 gram of substance gave 0·0574 gram H_2O and 0·2744 gram CO_2.

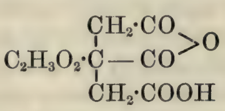
II. 0·1360 gram of substance gave 0·0455 gram H_2O and 0·2210 gram CO_2.

III. 0·2045 gram of substance gave 0·0682 gram H_2O and 0·3340 gram CO_2.

	Calculated for $O_8H_8O_7$.	Found.		
		I.	II.	III.
C	44·44	44·20	44·31	44·54
H	3·70	3·76	3·71	3·70

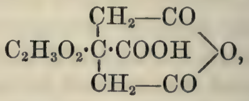
The three analyses were performed on different preparations; III had been recrystallised from ether.

The method of formation and reactions of the new compound show it to be acetanhydrocitric acid,



$$\begin{array}{l} \qquad\qquad CH_2{\cdot}CO \\ C_2H_3O_2{\cdot}C - CO \end{array}\!\!>\!O \quad \begin{array}{l} \\ \\ \qquad\qquad CH_2{\cdot}COOH \end{array}$$

or



$$\begin{array}{l} \qquad\qquad CH_2{-}CO \\ C_2H_3O_2{\cdot}C{\cdot}COOH \\ \qquad\qquad CH_2{-}CO \end{array}\!\!>\!O,$$

the former formula being the more probable. If boiled with excess of dilute potash, the substance behaved as a quadribasic acid.

0·3195 gram neutralised 5·9 c.c. normal KOH; calculated = 5·8 c.c.

After treatment with potash and careful neutralisation with nitric acid, a silver salt was precipitated; it contained 63·49 per cent. of silver. Silver citrate contains 63·15 per cent.

Acetanhydrocitric acid melts sharply at 115° (uncorr.), and is sparingly soluble in benzene, but very readily in ether, and on allowing the ethereal solution to evaporate spontaneously, it is deposited in groups of short prisms. The yield is very satisfactory, 153 grams of citric acid giving 149 grams of anhydride, and a further quantity can be obtained from the mother liquor.

Action of Heat.

Anschütz (*loc. cit.*) has shown that acetomalic anhydride distils unchanged in a vacuum, but that under ordinary pressure complete decomposition into acetic acid and maleic anhydride takes place. Acetoanhydrocitric acid might similarly be expected to furnish acetic and anhydroaconitic acids. As a matter of fact, however, we were unable to prepare the last named compound in this way, though it was easily obtained by the action of acetyl chloride on aconitic acid (see below).

As already mentioned, the acetanhydrocitric acid melts at 115° to a colourless liquid, at 150° decomposition takes place with evolution of acetic acid and carbon dioxide, whilst at 200° the decomposition is very rapid indeed, but ceases after a time, leaving a residue consisting of a brown oil. This distilled uniformly between 210° and 212°, and came over as a pale-yellow liquid having the characteristic odour of citraconic anhydride. A small quantity was warmed with water, and the solution allowed to cool, when crystalline plates of citraconic acid were deposited.

Analysis :—

0·099 gram of substance gave 0·0395 gram H_2O and 0·1665 gram CO_2.

	Calculated for $C_5H_6O_4$.	Found.
C	46·15	45·85
H...........	4·61	4·43

The decomposition had evidently taken place according to the equation

$$C_8H_8O_7 = CO_2 + C_2H_4O_2 + C_5H_4O_3.$$

The acetic acid produced in one operation was collected and weighed: 7·5 grams of the anhydride gave 2 grams of acetic acid, boiling at 110—120°. Theoretical yield = 2·08 grams.

Analysis of the silver salt of the acid gave 64·63 per cent. Ag. Calculated = 64·67.

The yield of re-distilled citraconic anhydride was 20 per cent. of the theoretical.

If the acid is distilled in a vacuum (30 mm.), the only difference in the result obtained is that itaconic anhydride is produced instead of citraconic; the itaconic anhydride was recrystallised from chloroform, and showed the m. p. 68—70°. Upon analysis :—

I. 0·1159 gram of substance gave 0·2260 gram CO_2 and 0·0372 gram H_2O.

II. 0·1378 gram of substance gave 0·2633 gram CO_2 and 0·0430 gram H_2O.

	Calculated for $C_5H_4O_3$.	Found.	
		I.	II.
C	53·57	53·18	53·10
H	3·57	3·56	3·47

Acetocitric Acid.

This is easily obtained by dissolving the anhydride in lukewarm water and evaporating the filtered solution in a vacuum over sulphuric acid; a colourless syrup remains which soon deposits the acid in hard, shining crystals; these melted at 138—140°, were very soluble in water, and gave the following results upon analysis:—

0·1713 gram of substance gave 0·0661 gram H_2O and 0·2564 gram CO_2.

	Calculated for $C_8H_{10}O_8$.	Found.
C	41·02	40·82
H	4·27	4·29

We were unable to obtain any characteristic salts of the acid. The silver salt blackened rapidly, even when precipitated from faintly acid solutions.

Action of Aniline on Acetanhydrocitric Acid.

If a solution of the acid in anhydrous ether is added drop by drop to a solution of aniline ($2\frac{1}{2}$ mols.) also in dry ether, an amorphous, deliquescent mass separates; this may possibly be regarded as an aniline salt of acetocitranilic acid. The crude product, when dried in a vacuum over sulphuric acid, was a brittle, pumice-like mass, and gave the following numbers on analysis:—

	Calculated for $C_{20}H_{22}N_2O_7$.	Found.
C	59·7	59·2
H	5·2	5·7
N	6·9	6·0

The substance is insoluble in ether, but dissolves readily in water, alcohol, and ethereal solution of aniline. The aqueous solution deposits crystals after a few days, and the ethereal aniline solution deposits a large quantity of crystalline matter if kept for a short time at the temperature of boiling ether. The crystals from both sources, when recrystallised from alcohol, showed the m. p. 180—182°, and on analysis were found to be citrodianilic acid.

I. (From ether-aniline.) 0·1150 gram of substance gave 0·0556 gram H_2O and 0·2655 gram CO_2.

II. (From ether-aniline.) 0·1267 gram of substance gave 9·25 c.c. N at 20° and 757 mm.

III. (From water.) 0·1629 gram of substance gave 11·75 c.c. N at 19° and 760 mm.

	Calculated for $C_{18}H_{18}N_2O_5$.	Found.		
		I.	II.	III.
C	63·18	62·94	—	—
H	5·26	5·35	—	—
N	8·12	—	8·36	8·15

The melting point of citrodianilic acid is, however, usually stated to be about 153° (Pebal, *Annalen*, **82**, 87). Recognising the possibility of at least two isomeric dianilic acids of the above formula, we prepared citrodianilic acid according to Pebal's directions; it was in appearance just like that which we obtained from the acetyl anhydride, and melted at 183°, so that the two substances must be considered as identical. Possibly 153° is a misprint for 183°.

Conversion of the Anhydro-acid into Aconitic Acid.

The ease with which acetic acid is removed from the acetyl anhydrides by the action of heat, suggested that alkalis might decompose these anhydrides in a similar manner with formation of unsaturated derivatives. In the case of the acetanhydrocitric acid, the reaction gives excellent results, and we propose to apply it to other acetyl derivatives in order to ascertain whether it is to be regarded as a general method for the production of unsaturated compounds.

10 grams of the acetyl derivative were dissolved in a small quantity of 96 per cent. alcohol, and allowed to fall drop by drop into a boiling solution of 20 grams of potash in 100 c.c. of alcohol. After all the acetyl derivative had been added, the solution was boiled for a few minutes and then allowed to cool; a slight yellow precipitate separated, but this was neglected. The liquid was now strongly acidified with hydrochloric acid, allowed to stand for a short time, and filtered from the precipitate of sodium chloride. Water was then added, the excess of alcohol removed by distillation, and the aqueous solution evaporated to dryness and extracted with ether.

After removing the ether by distillation, and recrystallising the residue from hot water, with addition of pure animal charcoal, a colourless product was obtained, crystallising in minute needles.

The analytical results showed it to be aconitic acid; the yield was 80—85 per cent. of the theoretical.

0·1719 gram of substance gave 0·0555 gram H_2O and 0·2587 gram CO_2.

	Calculated for $C_6H_6O_6$.	Found.
C	41·37	41·04
H	3·45	3·58

The melting point was found to be 190° (uncorr.), which is higher than that given in the text-books; it agreed, however, with that which we found for a recrystallised specimen of Kahlbaum's aconitic acid. Claisen and Höri (*Ber.*, **24**, 126) give the melting point of synthetical aconitic acid as 191°.

This is probably the most satisfactory method at present known for the preparation of aconitic acid; it is unnecessary to purify the acetanhydrocitric acid before treatment with potash, the original syrup obtained by the action of acetyl chloride on citric acid being sufficiently pure for the purpose.

Citrazinic Acid.

When an excess of strong ammonia (sp. gr. 0·880) is added to acetanhydrocitric acid, a slight rise of temperature takes place, and a clear solution is obtained; but no condensation occurs even if the solution is kept in sealed tubes for several weeks. If, however, the solution is heated at 120—130° for a couple of hours, the liquid assumes a reddish tint and becomes fluorescent; on boiling off the excess of ammonia and acidifying with hydrochloric acid, a light yellow precipitate is formed, which, after being redissolved in ammonia, filtered, and reprecipitated by acid, gave numbers which agree well with those required for citrazinic acid, $C_6H_5NO_4$.

0·1771 gram of substance gave 0·0520 gram H_2O and 0·3010 gram CO_2.

0·2280 gram of substance gave 18·4 c.c. N at 18° and 760 mm.

	Calculated for $C_6H_5NO_4$.	Found.	
		I.	II.
C	46·45	46·35	—
H	3·23	3·25	—
N	9·03	—	9·32

The sparing solubility of the substance in water, insolubility in alcohol, and the ready solubility in alkaline liquids, the intense blue fluorescence which such solutions show, and finally the brilliant blue coloration which the substance gives with a warm dilute solution of potassium nitrite, show the identity of the compound with the citrazinic acid of Behrmann and Hoffman. The yield is 35—40 per cent. of the anhydro-acid taken.

Attempts to effect a similar condensation by means of a concentrated solution of ethylamine were unsuccessful even when temperatures above 200° were employed. The solutions gave no precipitate with hydrochloric acid, but after removal of excess of ethylamine by a current of steam, and adding silver nitrate, a precipitate was obtained which contained a considerable percentage of nitrogen, showing the probable presence of an ethyl amic acid; as, however, the silver salts obtained were not constant in composition, the investigation was not followed up (compare Ruhemann, Trans., 1887, **51**, 408).

The fact that the anhydro-acid when heated with ammonia yielded citrazinic acid, but does not do so in the cold, suggests that an amic acid is first formed, which subsequently undergoes condensation. In order to satisfy ourselves as to whether citramic derivatives would condense under similar circumstances, we heated (α) citramide and (β) the mixture of citramic acids which is left as mother liquor in the preparation of citramide, each with ammonia of 0·880 at 120—130°. In each case, a good yield of citrazinic acid was obtained; the absence of citrazinamide, which might have been expected to be produced, is indicated by the analyses:—

(α.) 0·1146 gram of substance gave 9·6 c.c. N at 759 mm. and 21°.
(β.) 0·1611 „ „ 12·7 „ 759 „ 19·5°.

	Calculated for $C_6H_5NO_4$.	Found. (α.)	Found. (β.)
N	9·03	9·5	9·08

Similarly, methyl citrate was found to yield citrazinic acid when heated with ammonia in a sealed tube; the yield was 33 per cent. of the citric salt taken.

Reduction of Acetocitric Acid.

Regarding acetocitric acid as an ethereal salt, it appeared possible that by the action of reducing agents it might be directly converted into tricarballylic acid. Hitherto, however, we have been unable to effect this reduction, for, though a solution of acetocitric acid readily unites with hydrogen when acted on with sodium amalgam, the chief product of the reduction appears to be an uncrystallisable syrup easily soluble in water and alcohol, comparatively sparingly soluble in ether. We hope to return to this question in a subsequent communication.

The Anhydride of Aconitic Acid.

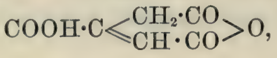
This compound is readily prepared by boiling aconitic acid with excess of acetyl chloride until complete dissolution is effected. On evaporating the filtered solution in a vacuum over solid potash, the anhydride gradually separates in colourless octahedra. The anhydride thus prepared is a hygroscopic substance melting at 95°; it is easily soluble in ether, alcohol, and hot benzene, from which it separates, on cooling, in modified cubes. On analysis:—

0·1745 gram of substance gave 0·0405 gram H_2O and 0·2904 gram CO_2.

	Calculated for $C_6H_4O_5$.	Found.
C................	45·56	45·43
H................	2·53	2·57

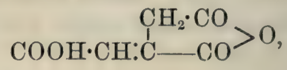
There are three possible formulæ, any one of which might represent the constitution of this anhydride :—

I.



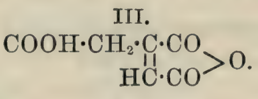
$$\mathrm{COOH{\cdot}C}\Big<\begin{matrix}\mathrm{CH_2{\cdot}CO}\\ \mathrm{CH{\cdot}CO}\end{matrix}\Big>\mathrm{O},$$

II.



$$\begin{matrix} & \mathrm{CH_2{\cdot}CO} \\ \mathrm{COOH{\cdot}CH{:}} & \mathrm{C\text{——}CO} \end{matrix}\Big>\mathrm{O},$$

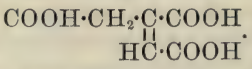
III.



$$\begin{matrix}\mathrm{COOH{\cdot}CH_2{\cdot}C{\cdot}CO} \\ \mathrm{HC{\cdot}CO}\end{matrix}\Big>\mathrm{O}.$$

Of these, formula I is improbable, since anhydrides approaching this type are almost unknown ; at the same time, the easy conversion of the anhydride into citrazinic acid, a pyridine derivative, might, perhaps, be taken as an argument in favour of this formula. Formula III would seem more probable than formula II, for III would represent the compound as a derivative of maleïc anhydride, II as a derivative of succinic anhydride. Substituted maleïc anhydrides are, as a rule, more easily formed than the corresponding succinic derivatives (compare especially diethylsuccinic and diethylmaleïc acids).

If, then, we regard the anhydride as a maleïc derivative, we must regard the acid which is formed by the action of water also as a maleïc derivative, that is, of quasi plane-symmetrical structure,



$$\begin{matrix}\mathrm{COOH{\cdot}CH_2{\cdot}C{\cdot}COOH} \\ \mathrm{HC{\cdot}COOH}\end{matrix}.$$

The anhydride readily unites with water, and passes thereby into ordinary aconitic acid (melting at 190°), which is therefore to be regarded as "maleoïd" aconitic.* We have attempted, but hitherto without success, to prepare the isomeric "fumaroïd" modification. Possibly the maleoïd form is so much more stable than the fumaroïd that the latter cannot be isolated. We hope to follow this interesting line of inquiry to a more definite conclusion.

Action of Ammonia on Aconitic Anhydride.

When dry gaseous ammonia is passed into a solution of the anhydride in dry ether, an amorphous, hygroscopic precipitate is formed which appears to be the ammonium salt of aconitodiamic acid.

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* Michael (*Ber.*, **19**, 1382) has come to practically the same conclusion from the reactions of the acid with aniline.

0·2428 gram of substance gave 46·15 c.c. N at 20° and 763 mm.

	Calculated for $C_6H_{11}N_3O_4$.	Found.
N	22·2	21·80

When this substance, which is deliquescent, is dissolved in ammonia of 0·880, or, indeed, if aconitic anhydride itself is dissolved in the same liquid, a solution is obtained which becomes fluorescent after a time, showing that condensation is slowly taking place. If the liquid is heated in a sealed tube for a couple of hours at 120°, the reaction takes place more rapidly, and, on acidifying the contents of the tube after the excess of ammonia has been removed, a precipitate of citrazinic acid is formed.

1·5 grams of the anhydride thus gave 0·23 gram of citrazinic acid, that is, 20 per cent. of the theoretical yield.

0·851 gram of substance gave 7·6 c.c. N at 20° and 765 mm.

Calculated for $C_6H_5NO_4$.	Found.
9·03	9·10

The acid showed the characteristic blue fluorescence in alkaline solution, and deep blue coloration with a warm dilute solution of potassic nitrite.

The anhydride of tricarballylic acid has recently been prepared by Emery (*Ber.*, **24**, 596), who has, moreover, shown that, by the action of gaseous ammonia on an ethereal solution of the anhydride, the ammonium salt of tricarballylamic acid is formed. It appeared possible that by the action of strong aqueous ammonia on this anhydride, a condensation might be effected as in the case of aconitic anhydride. We were, however, unable to effect such a condensation. The anhydride was heated at 140° and afterwards at 180° for several hours with an excess of concentrated ammonia, but no darkening of the solution occurred, and nothing was precipitated from the liquid on acidifying it with hydrochloric acid. On evaporating the ammoniacal solution upon the water-bath, an uncrystallisable syrup remained; this was dissolved in water and silver nitrate added, when a flocculent precipitate containing nitrogen was thrown down. Its composition was not constant, and it is probably a mixture of the salts of tricarballylic and tricarballylamic acids.

This difference between the reactions of the anhydrides of acids so nearly related as aconitic and tricarballylic is interesting, and seems to point to the fact that the formation of citrazinic acid from ethereal salts of citric acid is largely dependent on the easy formation of an "ethylene" linking.

Several points in connection with the anhydrides which we have dealt with in this paper have still to be worked out. Notably the action of ammonia and the effect of heat on these compounds require more careful study than we have hitherto had time to give to them. Phenylhydrazine, too, acts readily on the substances in question, producing crystalline derivatives, which we have not yet investigated. We hope, in a subsequent paper, to deal with these and some other points of interest which have arisen during the course of this investigation.

We desire, in conclusion, to express our thanks to Mr. T. T. Knowles and Mr. P. Hudson for the willing assistance they have afforded us in connection with the above work.

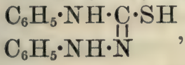
University Laboratory,
Cambridge.

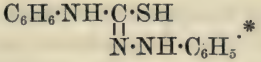
LXXXV.—*Di-substituted Semithiocarbazides.*

By AUGUSTUS E. DIXON, M.D., Professor of Chemistry, Queen's College, Cork.

IN two papers communicated to this Society (Trans., 1889, **55**, 302; and 1890, **57**, 257), I described experiments establishing the existence of isomeric forms amongst the di-substituted semithiocarbazides; and in the later of these papers, a suggestion was thrown out regarding a possible connection between the melting points and structure of this class of compounds. The study whose commencement is there recorded has been continued; but as it is still incomplete, it was my intention to refrain from publishing until the investigation could be further extended. A communication has, however, just appeared in the *Berichte* (1892, 3098), which touches so closely on the work in question, that I think it well to now lay before the Society an account of the principal experimental data already acquired.

The variety and intensity of the colour changes which take place on treating solutions of the semithiocarbazides with mineral acids, salts, and oxidising agents are very striking; amongst these are: crimson, blood-red, scarlet, orange, yellow, bright green, Prussian green, Prussian blue, azure blue, indigo, in addition to bottle green, olive, mahogany brown, and others. The colour changes are so remarkable, and often so characteristic, that I have recorded them in some detail.

W. Marckwald—the author of the paper above mentioned—has observed that the di-substituted semithiocarbazides appear to be capable of existing each in two forms; and since his experiments lead him to believe that these cannot be tautomeric, he explains their existence by supposing them to be stereoisomeric compounds, representing the (diphenylated) variety of lower melting point by the formula  $\begin{array}{rl} C_6H_5\cdot NH\cdot & C\cdot SH \\ & \| \\ C_6H_5\cdot NH\cdot & N \end{array}$, that of higher melting point being



$$\begin{array}{rl} C_6H_6\cdot NH\cdot & C\cdot SH \\ & \| \\ & N\cdot NH\cdot C_6H_5 \end{array}.^*$$

My own observations confirm those of Marckwald, so far at least as the frequent production of compounds of markedly different melting point is concerned. But in all the cases recorded below, except the benzylated derivatives, the substance described (where evidence of the presence of more than one was forthcoming) is that obtained by recrystallisation repeated until the compound of higher melting point alone appeared to be present.

Paratolylthiocarbimide and Phenylhydrazine.—Paratolylphenylsemithiocarbazide.

On mixing hot alcoholic solutions of the constituents in molecular proportion, crystals soon began to separate, and, on cooling, the whole set to a nearly colourless mass; this, after being drained on the filter-pump and well washed with alcohol, sintered at 149° (uncorr.). By repeated recrystallisation from alcohol, the substance was obtained in colourless, vitreous prisms melting at 173—174° (uncorr.), with effervescence, to a greenish brown liquid.

As indicated by the result of a sulphur determination, the compound is the expected semithiocarbazide:—

0·2144 gram of substance afforded 0·1952 gram $BaSO_4$.

	Calculated for $C_{14}H_{15}N_3S$.	Experiment.
S........	12·44 per cent.	12·51 per cent.

The material softening at 149° and that melting at 174° are, doubtless, respectively identical with Marckwald's "α-phenylparatolylthiosemicarbazid" sintering at 150°, and the corresponding

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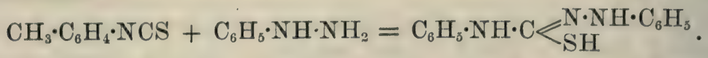
* The compound of lower, is converted into that of higher, melting point, according to Marckwald, not only by continued boiling of the alcoholic solution, but also by the addition to a boiling alcoholic solution of a trace of hydrochloric acid.

"β-" modification melting at 176°. The interaction may be thus formulated:—



$$CH_3{\cdot}C_6H_4{\cdot}NCS + C_6H_5{\cdot}NH{\cdot}NH_2 = C_6H_5{\cdot}NH{\cdot}C{<}^{N\cdot NH\cdot C_6H_5}_{SH}.$$

Paratolylphenylsemithiocarbazide is insoluble in water, rather sparingly soluble in benzene and in boiling alcohol, still less so in cold, easily in chloroform and in ether.

A dilute alcoholic solution, when treated with a few drops of ferric chloride, becomes deep bottle green, changing on heating to a mahogany red. Copper sulphate produces, even in very dilute solutions, an intense deep green coloration, which is not altered by heating. With solution of bleaching powder, a crimson coloration is produced, and on adding excess, a precipitate forms containing all the colouring matter. Neutral or ammoniacal silver nitrate produces a white, curdy precipitate which blackens almost instantaneously; but only a trifling desulphurisation occurs even on prolonged boiling with alkaline solution of lead. The substance is very stable towards mineral acids: on boiling with concentrated hydrochloric or dilute sulphuric acid, rendering alkaline, and heating with Fehling's solution, no cuprous oxide is formed. Cold concentrated nitric acid attacks the solid, the mixture becoming deep orange-red, and it dissolves readily in strong sulphuric acid, with production of a rich Prussian blue coloration.

Phenylthiocarbimide and Paratolylhydrazine.—Phenylparatolylsemithiocarbazide.

This was obtained by mixing the base and thiocarbimide in molecular proportion in alcohol, and heating the solution to its boiling point. On cooling, a crystalline mass was produced, which, after washing with spirit, sintered at about 117°. After three recrystallisations from alcohol, a substance was obtained in beautiful rosettes of feathery needles, perfectly colourless, becoming, when dry, highly electrical on friction, and melting with effervescence at 172° (uncorr.) to a clear, brownish liquid.

A sulphur determination gave the following result:—

0·2179 gram of substance afforded 0·1998 gram $BaSO_4$.

	Calculated for $C_{14}H_{15}N_3S$.	Experiment.
S	12·44 per cent.	12·60 per cent.

The substances sintering at 117° and melting at 172° are evidently identical with Marckwald's "α-" and "β-" modifications, the melting points of which he records as 123° and 175° respectively.

Phenylparatolylsemithiocarbazide is practically insoluble in boiling water, somewhat sparingly soluble in boiling alcohol, much less so in cold; soluble also in benzene, chloroform, and ether.

The solution in dilute alcohol gives with copper sulphate a deep, greenish black coloration, unchanged by boiling; with ferric chloride, a dark, greenish brown, becoming orange-yellow on heating; and with solution of bleaching powder, a beautiful scarlet coloration. Neutral and ammoniacal silver nitrate throw down curdy, whitish precipitates; that from the former blackens on standing for a short time in the cold; that from the latter passes almost instantly to full black. But the desulphurisation by alkaline solution of lead is trifling, and only occurs after boiling for some time. Cold nitric acid at once decomposes the solid substance, and a red oil separates. Unlike its metamer, previously described, it dissolves in cold concentrated sulphuric acid without change of colour; if the solution is heated, it becomes brownish.

Orthotolylthiocarbimide and Paratolylhydrazine.—Orthotolylparatolylsemithiocarbazide.

When prepared by very gently warming its constituents in alcohol, the principal product was a substance crystallising in white prisms, and melting at 130—131°, but immediately resolidifying; the resolidified substance showed a melting point of 162—163°. By repeated recrystallisation, a comparatively small quantity of a substance melting at 162—163° (uncorr.) could be obtained; but on combining the base with the hydrazine in boiling alcohol, the latter compound was obtained almost pure, and, after recrystallisation, formed long, fine, vitreous prisms melting sharply at 162—163°, with effervescence, to a brownish liquid.

A sulphur determination was made, with the following result:—

0·2306 gram of substance afforded 0·1975 gram $BaSO_4$.

	Calculated for $C_{15}H_{17}N_3S$.	Found.
S	11·82 per cent.	11·77 per cent.

The semithiocarbazide is insoluble in water, moderately soluble in boiling alcohol, somewhat sparingly in cold.

Ferric chloride, when added to the dilute alcoholic solution, produces a blood-red coloration, changing rapidly to bright green. On warming, the mixture becomes, first, olive brown, and then clear orange-red. With copper sulphate, an intense Prussian green is produced, destroyed by boiling, with formation of a black precipitate. Silver nitrate throws down a white, curdy precipitate, which gradually darkens on standing; a similar result is produced by the ammoniacal nitrate, save that the precipitate blackens almost instantly. Desulphurisation occurs, to a limited extent, on prolonged boiling with alkaline lead solution. On treating the solid with nitric acid, it is at once attacked; the mixture becomes orange, and a deep red oil separates. These reactions are substantially the same as those of the metameric paratolylorthotolyl compound; it is distinguished, however, by its melting point, and by the fact that it dissolves without sensible colour change in concentrated sulphuric acid.

Paratolylthiocarbimide and Orthotolylhydrazine.—Paratolylorthotolylsemithiocarbazide.

Alcoholic solutions of the constituents were mixed in molecular proportion, and the mixture gently heated on the water-bath; the crimson coloured liquid, on cooling, deposited aggregates of crystals; the yield of these, after draining on the filter-pump and washing with spirit, amounted to over 66 per cent. of the theoretical. After repeated recrystallisation from alcohol, the substance was obtained in colourless, vitreous prisms, melting constantly with effervescence at 141—142° (uncorr.).*

On analysis, the following result was obtained:—

0·3385 gram of substance afforded 0·2950 gram $BaSO_4$.

	Calculated for $C_{15}H_{17}N_3S$.	Experiment.
S	11·82 per cent.	11·98 per cent.

The substance dissolves rather sparingly in boiling alcohol, still less so in cold; in boiling water it is practically insoluble. It is attacked on gently warming it with nitric acid, with production of a bright orange coloration; and dissolves in cold concentrated sulphuric acid to a beautiful Prussian green solution. Silver nitrate, when added to the alcoholic solution, produces a finely divided white precipitate, which slowly passes, through yellow and red, to black, leaving a speculum; with the ammoniacal nitrate, a whitish precipitate falls, which immediately blackens. On prolonged boiling with alkaline solution of lead, some desulphurisation occurs, and the sides of the tube become brilliantly plated. On the addition of excess of Fehling's solution, the mixture becomes black and turbid, but no cuprous oxide is formed on boiling; neither is it produced if the substance is previously boiled with concentrated hydrochloric acid for some time.

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* No evidence was observed in this case of the production of an α-modification that the above substance exists in the β-form appears both from the effervescence on fusion and from the fact that the melting point remains unchanged after boiling with a little hydrochloric acid.

With ferric chloride, the cold alcoholic solution gives a deep greenish red coloration; on heating, the mixture becomes turbid, and deep crimson. This effect is presumably due to oxidation, as treatment with bleaching powder and dilute hydrochloric acid produces a similar colour and turbidity. The addition of a few drops of copper sulphate produces, even in very dilute solutions, an intense Prussian green coloration.

In one of the communications already quoted (*ante*, p. 1012), attention was drawn to the melting points of certain semithiocarbazides derived from orthotolylhydrazine. The ethyl compound melts at 130°; on exchanging the ethyl group for phenyl, the melting point rises to 146°; and for the reasons there stated, it was anticipated that the substitution of tolyl for the phenyl group would probably still further raise it. I have now obtained the compound in question—diorthotolylsemithiocarbazide—and find that its melting point does lie higher than that of phenylorthotolylsemithiocarbazide, though only by a few degrees. The preparation and chief properties of this compound are described below.

Orthotolylthiocarbimide and Orthotolylhydrazine.—Diorthotolylsemithiocarbazide.

The constituents were heated in alcoholic solution in molecular proportion. A deep greenish brown liquid was the result, which, after standing for several hours, deposited a quantity of crystals. The latter, after repeated recrystallisation from alcohol, were obtained in aggregates of brilliant, colourless octahedra, insoluble in water, moderately soluble in boiling alcohol, somewhat sparingly in cold, and melting at 148—149° (uncorr.) with copious effervescence.

The substance, as indicated by the result of a nitrogen determination, is ditolylsemithiocarbazide:—

0·2208 gram of substance, burnt with copper oxide, afforded 28·7 c.c. of nitrogen, measured at 15·5° and 763·5 mm.

	Calculated for $C_{15}H_{17}N_3S$.	Experiment.
N........	15·53 per cent.	15·34 per cent.

When ferric chloride is added to an alcoholic solution, the mixture becomes intense blood-red; a like result follows on treatment with potassium dichromate and dilute sulphuric acid, or bleaching powder and dilute hydrochloric acid. A bright emerald green colour is produced by warming with potassium ferricyanide; and with copper sulphate, even in very dilute solutions, an intense deep green. A cold alcoholic solution is blackened instantly on the addition of ammoniacal silver nitrate; but the desulphurisation is very trifling (with production of a slight speculum), even after continued boiling with alkaline solution of lead. The solid substance, when treated with nitric acid, yields a deep bromine-coloured mixture; and it dissolves in cold sulphuric acid, producing a faint green coloration, which, on warming, changes to a rich claret.

The following compound completes the series of ortho- and paraditolyl derivatives of this class.

Paratolylthiocarbimide and Paratolylhydrazine.—Diparatolylsemithiocarbazide.

In this case, as in that of the corresponding ortho-para-compound, the nature of the product depends on the conditions under which it is obtained.

Operating in gently heated alcoholic solution, aggregates of flattened crystals are formed; these melt at temperatures, varying in different experiments, from 120° to 125°. The melted product rapidly solidifies again, and the melting point now rises to a temperature varying from 148° to 153°. In these cases, it was found impracticable, by recrystallisation, to separate a compound having the higher melting point.

The second modification was, however, easily obtained by mixing boiling alcoholic solutions of the constituents; the product, after a couple of recrystallisations from the same solvent, formed tufts of pointed prisms, melting sharply with effervescence, to a yellowish-green liquid, at 153·5—154° (uncorr.).*

On analysis, a compound having a primary melting point of 124—125° gave the following result:—

0·2268 gram of substance afforded 30·8 c.c. of moist nitrogen, measured at 16° and 768·5 mm.

A compound melting at 153—154° was also analysed:—

0·2035 gram of substance yielded 0·1680 gram $BaSO_4$.

	Calculated for $C_{15}H_{17}N_3S$.	Experiment.
N	15·53 per cent.	16·00 per cent.
S........	11·82 ,,	11·35 ,,

These two substances are, accordingly, both diparatolylsemithiocarbazides; probably the former corresponds to Marckwald's α-, and the latter to his β-diphenyl derivative.

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* The latter melting point was unchanged after boiling the substance with a little hydrochloric acid.

Diparatolylsemithiocarbazide, m. p. 154°, is insoluble in water, freely soluble in hot alcohol, but much less so in cold; easily in ether, chloroform, and benzene. Cold nitric acid vigorously attacks the solid, yielding a mahogany brown solution; and it dissolves in concentrated sulphuric acid, producing an olive green coloration, which, on warming, changes to brownish red.

The alcoholic solution gives, with copper sulphate, a deep green colour, unchanged by heating; with bleaching powder, a bright vermilion precipitate; with potassium ferricyanide, a clear yellow, becoming deep orange-yellow on warming; and with ferric chloride, a greenish red, gradually changing to greenish brown. If the latter solution be heated, it turns bright orange-yellow. Neutral or ammoniacal silver nitrate yields a whitish precipitate, which gradually blackens in the cold; and the substance is desulphurised, though incompletely, by continued boiling with alkaline solution of lead.

α-Naphthylthiocarbimide and Phenylhydrazine.—α-Naphthylphenylsemithiocarbazide.

The preparation of this compound was undertaken in order to compare its properties with those of Freund's (*Ber.*, **24**, 4190) phenylthiocarbimide and α-naphthylhydrazine product. Molecular proportions of the constituents were mixed in hot alcoholic solution, and in a few minutes the contents of the vessel solidified to a pure white, crystalline mass, the weight of which, after draining, washing with spirit, and drying, amounted to over 93 per cent. of that of the materials employed. By recrystallisation from alcohol, it was obtained in brilliant, vitreous needles, melting with copious effervescence at 183° (uncorr.).

Sulphur determination:—

0·3979 gram of substance yielded 0·3172 gram $BaSO_4$.

	Calculated for $C_{17}H_{15}N_3S$.	Experiment.
S........	10·93 per cent.	10·97 per cent.

The substance is insoluble in water, rather sparingly soluble in boiling alcohol, ether, or benzene, somewhat more easily in chloroform. Ammoniacal nitrate of silver, when added to the alcoholic solution, throws down a white, curdy precipitate, which is stable in the cold, but blackens very readily on gently warming; on boiling with alkaline solution of lead, desulphurisation is slowly and imperfectly effected. With ferric chloride, the alcoholic solution gives an orange coloration, scarcely altered by heating; copper sulphate produces an intense green, unchanged by boiling; and bleaching powder a scarlet coloration. The solid is attacked vigorously by nitric acid, with production of a scarlet oil; and it dissolves in sulphuric acid, giving a straw yellow solution, which, on heating, becomes at first somewhat paler, and darkens at a high temperature, owing to carbonisation.

As already stated, the substance melts at 183°, and is, therefore, isomeric with Freund's phenyl-α-naphthyl derivative, melting at 135°.

Phenyl-β-naphthylsemithiocarbazide.

According to Freund (*loc. cit.*, p. 4180), this substance (prepared from phenylthiocarbimide and β-naphthylhydrazine), forms white leaves, easily soluble in alcohol, and melting at 202°. My own results differ somewhat from the above, as the substance I obtained from these materials occurred, after repeated crystallisation from spirit, in very delicate, flexible, pearly needles, by no means freely soluble in alcohol, and melting, with much effervescence, at 184—184·5° (uncorr.).

A nitrogen determination was made in order to check the formula.

0·2020 gram of substance afforded 25·5 c.c. moist nitrogen at 17° and 751 mm., or N = 14·46 per cent.

Calculated for $C_{17}H_{15}N_3S$, N = 14·36 per cent.

To his description, the following may be added:—The alcoholic solution gives with ammoniacal silver nitrate a black precipitate, but is not sensibly desulphurised by boiling with alkaline solution of lead. Copper sulphate produces a deep green precipitate, soon becoming black; ferric chloride an orange coloration, changing on warming to deep brownish red; and bleaching powder a rich red, almost scarlet, precipitate. The solid is attacked by nitric acid with formation of a bromine-coloured, oily liquid; and dissolves in sulphuric acid, yielding a clear, yellowish green solution, which on warming becomes cherry-red. The solution in alkali, when boiled and treated with copper sulphate, yields no cuprous oxide.

β-Naphthylthiocarbimide and Phenylhydrazine.—β-Naphthylphenylsemithiocarbazide.

This isomer of the preceding was prepared from its constituents in hot alcoholic solution; when recrystallised from alcohol, it forms delicate, silvery needles melting at 190—191° (uncorr.).

On analysis, the following data were obtained:—

0·2205 gram of substance afforded 0·5628 gram CO_2 and 0·1124 gram H_2O.

	Calculated for $C_{17}H_{15}N_3S$.	Experiment.
C........	69·57 per cent.	69·60 per cent.
H........	5·13 ,,	5·67 ,,

It is insoluble in water, rather sparingly soluble in boiling alcohol, and still less so in cold.

Silver nitrate produces a white precipitate, soon darkening; with the ammoniacal nitrate, the mixture blackens at once; but no desulphurisation occurs on boiling with alkaline solution of lead. A dilute alcoholic solution gives with ferric chloride a mahogany red coloration, not affected by heating; with copper sulphate, a deep greenish black; and with bleaching powder and hydrochloric acid, a clear light orange. The solid is vigorously attacked by nitric acid, with production of an intense crimson-coloured oil, and dissolves in sulphuric acid, yielding a clear green solution, which is bleached on warming.

No benzylated derivatives of the semithiocarbazides appear as yet to have been recorded. I have therefore taken the present opportunity of extending our knowledge of this class of substances by the preparation of the compounds described below.

Benzylthiocarbimide and Phenylhydrazine.—Benzylphenylsemithiocarbazide.

This is prepared by warming its constituents together in alcoholic solution, and, after several recrystallisations from alcohol, is obtained in beautiful tufts of white, flexible prisms, melting between 115° and 116°.* The yield amounted to about 70 per cent. of the theoretical.

A portion was dried over sulphuric acid and the nitrogen estimated:—

0·1876 gram of substance, burnt with copper oxide, afforded 26·6 c.c. of nitrogen, measured at 16° and 763 mm.

	Calculated for $C_{14}H_{15}N_3S$.	Experiment.
N........	16·38 per cent.	16·59 per cent.

Benzylphenylsemithiocarbazide, when heated with water, melts to an oil which sinks in the liquid. A trace dissolves in the boiling water, but, when the temperature is allowed to fall, the liquid becomes turbid from the separation of oily globules, which after a time again solidify. It is moderately easily soluble in hot alcohol, sparingly in cold.

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* Since the above was written, I have observed that this substance, when boiled with a trace of hydrochloric acid (as recommended by Marckwald), exhibits a melting point of about 163°. The compound described is, therefore, probably the α-modification.

The solid substance is not readily attacked by cold nitric acid, but, on gentle warming, action commences; oxides of nitrogen are evolved, and the liquid contents of the tube become mahogany red. The pure substance dissolves in concentrated sulphuric acid with a clear, brown colour. On the addition of copper sulphate to the dilute alcoholic solution, an intense greenish blue coloration is produced, which is not affected by boiling; with ferric chloride, a fine blood-red coloration appears, which, as the oxidation proceeds, slowly changes to greenish brown. If Fehling's solution is mixed with that of the substance, and heat applied, the mixture simply blackens; but if the substance is previously boiled with hydrochloric acid, it undergoes more or less decomposition into its constituents; the cress-like odour of benzylthiocarbimide is noticeable, and the residual solution, if heated with Fehling's solution after treatment with excess of potash, gives a dark red precipitate of cuprous oxide.

Benzylthiocarbimide and Paratolylhydrazine.—Benzylparatolylsemithiocarbazide.

This compound was prepared from its constituents as above described. When purified by recrystallisation from alcohol, it formed colourless, shining, flattened prisms melting quietly at 120—121° and decomposing, with effervescence, at 166°. The melting point was not changed by boiling the alcoholic solution for a short time with hydrochloric acid, but the non-effervescence at the melting point seems to suggest that this is the α-modification.

The following result was obtained on analysis:—

0·2291 gram of substance yielded 32·2 c.c. of nitrogen, measured at 17° and 746 mm.

	Calculated for $C_{15}H_{17}N_3S$.	Experiment.
N........	15·53 per cent.	15·99 per cent.

Benzylparatolylsemithiocarbazide dissolves moderately freely in boiling alcohol, somewhat sparingly in cold, and is insoluble in water. Boiling with alkaline lead solution fails to desulphurise it; but with ammoniacal nitrate of silver, a curdy, white precipitate is produced, stable in the cold, but easily blackened on heating with formation of a speculum of silver sulphide. Neutral nitrate of silver does not cause a precipitate, but the mixture, on heating, becomes black, and a mirror is formed.

Copper sulphate, when added to the alcoholic solution, produces a bright green coloration, unaltered by boiling; ferric chloride, under like conditions, yields an intense deep red, and bleaching lime a clear yellow colour.

The solid substance dissolves in nitric acid, forming a yellowish solution, which on warming decomposes, evolving ruddy fumes and leaving an orange red liquid. It is soluble, without sensible colour change, in concentrated sulphuric acid; if this solution is heated, it becomes first amber yellow, and then bottle green. Like its lower homologue just described, it does not reduce alkaline copper tartrate even on boiling; but it is to some extent decomposed by continued boiling with strong hydrochloric acid; the residual solution, after treatment with excess of potash, is desulphurised to a slight extent by alkaline lead solution, and affords, when warmed with Fehling's reagent, a small quantity of cuprous oxide.

I have to thank Mr. D. J. O'Mahony for the help which he has rendered with a portion of the analytical work recorded in this paper.

LXXXVI.—*Studies on the Interaction of Bromine and Toluene. Preparation and Properties of Orthobromotoluene and Parabromotoluene, and of the Dibromotoluenes derivable therefrom. Ortho- and Para-bromotoluenesulphonic Acids.*

By ALEXANDER K. MILLER, Ph.D.*

THE experiments described in this paper were made chiefly with the view to determine the constitution of the dibromo-derivative or derivatives of toluene obtainable under certain definite conditions, and also to ascertain, as far as possible, the order in which the bromine atoms enter into the nucleus of the hydrocarbon when it is converted into higher bromo-derivatives.

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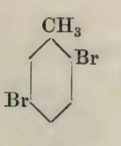
* The experiments here recorded were carried out by Dr. Miller prior to his departure from the Central Institution in June, 1888, when he accepted an industrial post. The publication of the results was deferred in order that the chain of evidence necessary to establish the constitution of the main product of sulphonation of orthobromotoluene might be completed; Dr. Wynne's experiments (see p. 1036) having supplied the necessary connecting link, it now appears advisable to make the results public.—HENRY E. ARMSTRONG.

Judging from the fact that mono-derivatives are practically the sole products obtained when toluene is submitted to the action of a molecular proportion of bromine, and that a second molecular proportion of the halogen acts with great sluggishness in comparison with the first, the assumption seems justifiable that the formation of a dibromo-derivative from toluene takes place in two distinct stages, the mono-derivative being first formed and subsequently converted into a di-derivative. Such being the case, experiments in which the monobromination products are first isolated, and each then separately submitted to the further action of bromine, might be expected to yield the same products—though in different proportions—as the direct treatment of the hydrocarbon with two molecular proportions of the halogen.

It is well known that the first action of bromine is to substitute hydrogen, both in the ortho- and para-positions to the methyl group; but its further action has never been satisfactorily studied. Many years ago, Fittig stated (*Annalen*, **147**, 40) that the bromination of toluene beyond the mono-stage takes place very sluggishly, the product after three weeks' action being a mixture of a solid dibromotoluene melting at 107—108° and a good deal of mono-bromotoluene. Fittig also stated that he could not obtain tribromotoluene by brominating at the atmospheric temperature.

Jannasch (*Annalen*, **176**, 286), hoping to obtain a better yield of dibromotoluene, submitted monobromotoluene (the mixture of ortho- and para- obtained on brominating toluene) to the action of bromine in the presence of iodine and under the influence of direct sunlight. The product described by him was a *liquid* which did not solidify even when surrounded by a freezing mixture. When treated with methyl iodide and sodium, it yielded pseudocumene, and from this Jannasch concluded that his dibromotoluene might have been a mixture of the three following isomerides:—



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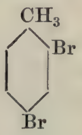

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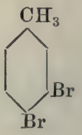

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(3)

If all three compounds were actually present in Jannasch's product, that represented by the first symbol must have been derived from orthobromotoluene, whilst the second isomeride might have been derived either from ortho- or from para-bromotoluene, or partly from each, the third isomeride, on the other hand, must have been derived only from parabromotoluene. Now, although Jannasch's experiments afford no clue as to whether one, two, or all three of the above isomerides were actually formed, and, as far as I am aware, no one else has published anything more definite on the subject, it nevertheless appears to be more or less generally assumed that the di-bromination product of toluene consists either chiefly or wholly of the 1 : 3 : 4-isomeride (Beilstein [2], **2**, 46; Fittig-Wöhler, 1887, 524). Beilstein, in fact, assigns this formula to Jannasch's product above referred to, though apparently without reason, and certainly not on Jannasch's authority, as the latter regarded his product as a mixture.

It will be seen that in the experiments which are described in this communication the conditions under which bromination took place differed somewhat from those adopted by Jannasch; and it is interesting that, in spite of this, the dibromotoluenes which I obtained were three in number, and that they corresponded with the isomerides whose formulæ are quoted above from Jannasch's paper.

With the view both to determine the constitution of the dibromo-products and to trace the formation of each through the monobromo-stage, the two mono-substitution products were first prepared in a state of purity and were then separately submitted to the further action of bromine.

Bromination of Toluene.

The hydrocarbon was obtained by hydrolysis from recrystallised potassium tolueneparasulphonate, and had a constant boiling point of 111—112°.

Both the toluene and the bromine were freed from water by agitation with sulphuric acid. *The bromination was conducted in a room from which daylight was carefully excluded*, the interaction being assisted by the addition of a crystal or two of iodine; and throughout the operation access of moisture was guarded against. The evolution of hydrogen bromide was vigorous at first, but gradually became more and more sluggish until, after about five or six days, there appeared to be no more action. The product was shaken with a dilute solution of caustic soda to remove bromine, and the oily layer was then distilled in a current of steam and fractionated; its odour, which was characteristic, and the fact that it did not irritate the eyes, indicated that it was free from benzyl bromide—a result which was undoubtedly ascribable to the care taken to exclude light. The crude mixture of ortho- and para-bromotoluenes was then subjected to the alternate action of a good freezing mixture and weakly-fuming sulphuric acid —the well-known method of separating the two isomerides. The separation of the isomerides effected in this manner, however, is by no means complete, so that an accurate determination of the relative proportions of the two could not be effected; but I have no hesitation in saying that in my experiments the para-derivative was produced in decidedly larger amount than the ortho-compound. Hübner and Post state (*Annalen*, **169**, 1) that they obtained about equal amounts of each.

Parabromotoluene.—An approximate purification of the product obtained as above indicated is readily effected by crystallising it from spirit; to complete its purification, it may advantageously be sulphonated; the sulphonic acid is purified by crystallisation of the lead, barium, or potassium salt, and the purified salt is then hydrolysed, and the product finally crystallised from spirit. Parabromotoluene was thus obtained in magnificent, colourless plates melting at 28·5°. It distilled at 185—185·5°.

The main product of the sulphonation of parabromotoluene yielded salts, of which the composition was found to be as follows:—

Potassium salt	$2C_7H_6BrSO_3K,H_2O$.
Barium salt	$(C_7H_6BrSO_3)_2Ba,2H_2O$.
Lead salt	$(C_7H_6BrSO_3)_2Pb,2H_2O$.

I. 0·3965 gram of potassium salt, dried at 150°, lost 0·0123 gram water.

II. 0·4950 gram of the salt lost 0·0152 gram water.

	Calculated for $2C_7H_6BrSO_3K,H_2O$.	Found. I.	Found. II.
H_2O	3·02 per cent.	3·10	3·07 per cent.

0·4521 gram of barium salt lost at 180° 0·0242 gram water.

	Calculated for $(C_7H_6BrSO_3)_2Ba,2H_2O$.	Found.
H_2O	5·35 per cent.	5·35 per cent.

0·3898 gram of lead salt lost 0·0190 gram water.

	Calculated for $(C_7H_6BrSO_3)_2Pb,2H_2O$.	Found.
H_2O	4·84 per cent.	4·87 per cent.

The last two salts have been described by Hübner and Post (*loc. cit.*) who, however, found 1 mol. H_2O in the barium salt and 3 mols. H_2O in the lead salt.

The mother liquor from which the dihydrated barium salt had been separated yielded a small quantity of an ill-defined anhydrous salt, whilst the corresponding salt, obtained by Hübner and Post, crystallised with 7 mols. H_2O.*

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* Dr. Wynne proposes to fully examine the minor products of sulphonation of both parabromo- and parachloro-toluene, as their nature is at present by no means satisfactorily determined.—H. E. A.

0·2862 gram of the salt lost nothing at 150°, and yielded 0·1017 gram $BaSO_4$.

	Calculated for $(C_7H_6BrSO_3)_2Ba$.	Found.
Ba........	21·50 per cent.	20·89 per cent.

Orthobromotoluene.—The purification of orthobromotoluene is a much less simple matter than that of its isomeride, there being no ready method of separating the last traces of the para-derivative. It was accordingly found advantageous to prepare it by a method which I briefly described in 1886 (Proc., 1886, 235), by which it can be obtained in a state very closely approximating to purity and free from either of its isomerides. As the method has only been partially described, a more detailed description may be now given.

Bromine in calculated quantity is added to a warm concentrated solution of pure potassium tolueneparasulphonate contained in a strong stoppered bottle (such as a bromine bottle). The mixture is heated at about 60—70° in a water-bath and repeatedly shaken. After three to four hours' treatment, the mixture, in which free bromine is still present, is put into a flask attached to a condenser, and a current of steam is passed through it. This not only removes the unabsorbed bromine, but also an oily product which separates during bromination; the residual solution contains potassium orthobromotolueneparasulphonate [$CH_3 : Br : SO_3K = 1 : 2 : 4$], some unaltered potassium tolueneparasulphonate, and potassium bromide. As the solution cools, the orthobromosulphonate crystallises out and is readily purified by recrystallisation; it sometimes has a yellowish tinge owing to the presence of a trace of a bromine compound of unknown composition, and to free it from this it should be crystallised from spirit, from which it separates in beautiful, white plates of the composition $C_7H_6BrSO_3K$.

I. 0·4943 gram of air-dried salt yielded 0·1470 gram K_2SO_4.
II. 0·4605 gram of the salt yielded 0·1357 gram K_2SO_4.

	Calculated for $C_7H_6BrSO_3K$.	Found. I.	Found. II.
K............	13·49 p. c.	13·33	13·25 p. c.

The barium salt crystallises in glistening plates of the composition $(C_9H_6BrSO_3)_2Ba,2H_2O$.

I. 0·4247 gram of the barium salt lost 0·0259 gram when dried, and yielded 0·1464 gram $BaSO_4$.
II. Same specimen, but recrystallised.—0·5500 gram lost 0·0317 gram water.

	Calculated for $(C_7H_6BrSO_3)_2Ba,2H_2O$.	Found.	
		I.	II.
H_2O	5·35 p. c.	6·09	5·76 p. c.
Ba (in anhydrous salt)	21·50 ,,	21·58	— ,,

The composition of the two salts agrees with the description (*Annalen*, **172**, 205) given by Hayduck of the orthobromotolueneparasulphonates which he prepared from orthamidotoluenesulphonic acid [$C_6H_3Me(NH_2)SO_3H$ = 1 : 2 : 4].

The other product of the bromination of potassium tolueneparasulphonate, namely, the oil separated by steam distillation, was freed from bromine and fractionally distilled. It was readily separated into mainly two fractions, one boiling at about 185° and the other above 240°, this higher portion decomposing partly on further distillation:—

I. Fraction boiling at about 185°.—This solidified on cooling, and was readily obtained in a pure state by redistillation and crystallisation from spirit. It was at once recognised as *parabromotoluene*, as it melted at 28·5° and distilled at 185°.

II. Fraction boiling above 240°.—This separated into a solid substance and an oil. The latter was obtained in too small quantity to allow of a complete examination. It was sulphonated, and analyses of its barium and potassium sulphonates indicated it to be a *dibromotoluene.*

0·5136 gram of barium salt lost 0·0327 gram water at 150°, and yielded 0·1409 gram $BaSO_4$.

	Calculated for $(C_7H_5Br_2SO_3)_2Ba,3H_2O$.	Found.
H_2O	6·36 p. c.	6·36 p. c.
Ba (in anhydrous salt)	17·23 ,,	17·23 ,,

0·3346 gram of potassium salt lost at 150° 0·0160 gram water, and yielded 0·0733 gram K_2SO_4.

	Calculated for $C_7H_5Br_2SO_3K,H_2O$.	Found.
H_2O	4·66 p. c.	4·78 p. c.
K (in anhydrous salt)	10·60 ,,	10·31 ,,

The solid product was readily recognised as *parabromobenzyl bromide;* it crystallised from alcohol in needles melting at 61°, and its odour and action on the eyes were those characterising a benzyl derivative. On heating it with silver nitrate solution, a precipitate of silver bromide was produced. A determination of the total bromine gave the following result:—

0·2130 gram of the substance yielded 0·3210 gram AgBr.

	Calculated for $C_6H_4Br{\cdot}CH_2Br$.	Found.
Br..........	64·00 p. c.	64·13 p. c.

From the above, it will be seen that the main products of the bromination of potassium tolueneparasulphonate are *potassium orthobromotolueneparasulphonate*, *parabromotoluene*, and *parabromobenzyl bromide.*

The orthobromosulphonate is readily freed from every trace of parabromotoluene in the manner indicated, and, on hydrolysing the purified salt, it affords an almost theoretical yield of orthobromotoluene of high quality.* The boiling point of a sample prepared in this manner was 181°, and its relative density $d\,15°/15° = 1·431$.

The *sulphonation of orthobromotoluene* has been studied by Hübner and Post (*Annalen*, **169**, 31), who state that only one sulphonic acid is obtained. In my experiments, I found that two isomeric sulphonic acids were invariably produced, whether ordinary pure oil of vitriol or weakly fuming sulphuric acid were employed. The main product was that obtained by Hübner and Post; its barium salt crystallised with two and its potassium with half a molecular proportion of water:—

0·4479 gram of barium salt lost 0·0250 gram water at 150°, and yielded 0·1549 gram $BaSO_4$.

	Calculated for $(C_7H_6BrSO_3)Ba,2H_2O$.	Found.
H_2O..................	5·35 p. c.	5·58 p. c.
Ba (in anhydrous salt) .	21·50 „	21·53 „

0·4829 gram of potassium salt lost 0·0149 gram water at 150°, and yielded 0·1363 gram K_2SO_4.

	Calculated for $2C_7H_6BrSO_3K,H_2O$.	Found.
H_2O	3·02 p. c.	3·08 p. c.
K (in anhydrous salt)...	13·49 „	13·06 „

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* According to Kelbe (*Ber.*, **19**, 93), bromotoluenesulphonic acid can only be hydrolysed when superheated steam is employed, the method failing completely when steam at 100° is used. This, however, is not the case when the operation is properly conducted. In my experiments, steam at 100° was invariably employed, and not only was there no carbonisation, but the yield of bromotoluene (both ortho- and para-) was very nearly quantitative, as will be seen from the following two examples:—76 grams of $C_6H_3MeBr{\cdot}SO_3K$ [1 : 2 : 4] yielded 41 grams of orthobromotoluene, the theoretical yield being 45 grams. 150 grams of $C_6H_3MeBr{\cdot}SO_3K,H_2O$ [1 : 2 : 5] yielded 82 grams of orthobromotoluene, the theoretical amount being 86 grams.

For further confirmation, the potassium salt was boiled with zinc-dust in alkaline solution; ultimately, the resulting toluenesulphonate was converted into the corresponding toluenesulphonamide: this crystallised in needles melting at 90—91° (toluenemetasulphonamide), thus confirming Hübner and Post's statement that in orthobromotoluenesulphonic acid, the sulphonic group is in the meta-position relatively to the methyl radicle. Whether it is ortho- or para- to the bromine atom I was unable to determine, but the most probable constitution would appear to be $CH_3 : Br : SO_3H = 1 : 2 : 5$.*

With the view to ascertain the position of the sulphonic group, an attempt was made to displace it by means of phosphorus pentabromide. The conversion into the sulphonic bromide was readily effected; the product crystallised in massive prisms melting at 58—59°. The further action of the pentabromide, however, gave rise to a viscid mass, from which nothing definite could be obtained.

The isomeric sulphonic acid is produced in but small quantity, and is best separated from the chief product by fractionally crystallising the barium salt; that of Hübner and Post's acid separates first.

The more soluble salt crystallised in minute scales, containing 1 mol. H_2O.

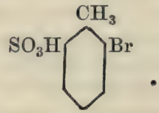
I. 0·3868 gram of barium salt lost 0·0105 gram water at 150°, and yielded 0·1391 gram $BaSO_4$.

II. 0·3668 gram lost 0·0098 gram water.

	Calculated for $(C_7H_6BrSO_3)_2Ba,H_2O$.	Found. I.	Found. II.
H_2O	2·75 p. c.	2·71	2·67 p. c.
Ba (in anhydrous salt)	21·50 ,,	21·73	— ,,

The corresponding potassium salt was anhydrous.

The constitution of this product was determined by eliminating the bromine and converting the resulting toluenesulphonic acid first into the sulphonic chloride and then into the sulphonamide. The former was an oil, whilst the latter was recognised by its melting point (154°) to be *tolueneorthosulphonamide.* The orthobromotoluenesulphonic acid from which this was obtained must therefore have the constitution



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* The results obtained by Dr. Wynne (see p. 1036) prove that the acid in question has the constitution here suggested as probable by Dr. Miller.—H. E. A.

Dibromotoluenes.

The bromination of the two monobromotoluenes was conducted under the same conditions as those observed in the bromination of toluene, except that a longer time was allowed owing to the sluggishness of the interaction.

Bromination of Orthobromotoluene.—27 grams of highly purified bromotoluene and the equivalent amount of bromine were allowed to interact for 10 days, at the end of which time action appeared to have ceased. The free bromine having been removed by agitating the product with dilute soda solution, the oil was separated, dried, and carefully fractionated. The distillates obtained were as follows :—

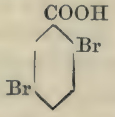
I.	Fraction distilling at	178--190°,	6·0 grams.
II.	" "	190—230°,	2·0 "
III.	" "	230—243°,	25·5 "

From this result it is evident that nearly three-quarters of the orthobromotoluene had become converted into a liquid dibromoderivative, the remainder being unaltered substance, whilst no tri-tribromotoluene appeared to have been formed.

In order to determine the nature of the product, the fraction distilling between 230° and 243° was oxidised by boiling it with dilute nitric acid (1 vol. acid of rel. den. 1·42 to 3·5 vols. water). A method of this kind is clearly not suited to the accurate determination of the relative amounts of isomerides should two or more dibromotoluenes be present, but I considered it sufficient to enable me to detect with certainty any great difference in the amount of the isomerides present in the mixed product.

The oxidation was carried on until all the oil had disappeared, and it was found that only a very small proportion had become nitrated.

The resulting dibromobenzoic acids were separated partly by crystallising their barium salts and partly by crystallising the acids. The main product was indicated by its properties to be



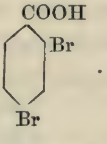
It crystallised from alcohol in silky needles melting at 153°. Its barium salt crystallised from its aqueous solution with 6 mols. H_2O, and from alcohol with $1\frac{1}{2}$ mols. H_2O.

I. Salt crystallised from water.—0·2861 gram lost 0·0401 gram in weight at 100°, and yielded 0·0849 gram $BaSO_4$.

II. Salt crystallised from spirit.—0·3017 gram lost 0·0100 gram.

	Calculated for $(C_6H_3Br_2COO)_2Ba,6H_2O$,	Found. I.	Found. II.
H_2O	13·45 p. c.	14·01	3·31 p. c.
	$(C_6H_3Br_2COO)_2Ba,1\frac{1}{2}H_2O$.		
H_2O	3·74 ,,	20·29	— ,,
Ba (in anhydrous salt)		19·71 per cent.	

An isomeric dibromobenzoic acid found in much smaller quantity than the above proved to be



It crystallised in needles melting at 169°. Its barium salt contained 4 mols. H_2O :—

0·3795 gram of the salt lost 0·0359 gram water at 120°, and yielded 0·1132 gram $BaSO_4$.

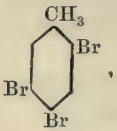
	Calculated for $(C_6H_3Br_2COO)_2Ba,4H_2O$.	Found.
H_2O	9·39 p. c.	9·46 p. c.
Ba (in anhydrous salt) .	19·71 ,,	19·37 ,,

From these results it is evident that under the conditions described orthobromotoluene is in greater part converted into dibromotoluenes, and that the bromination takes place in two directions: the greater tendency being for the substituent to displace the hydrogen atom in the para-position relatively to the bromine atom already present in the nucleus, and to a less extent that present in the para-position to the methyl group.

Bromination of Parabromotoluene.—This was carried out in the same manner as in the case of the ortho-compound, and the product was also treated as before. Although in this case a longer period, namely 18 days, was allowed for the bromination, the proportion of dibromotoluene produced was relatively smaller; the product contained a larger proportion of unaltered parabromotoluene and a very appreciable quantity of tribromotoluene:—

I. Fraction distilling below 195°, 19 grams.
II. ,, ,, at 195—235°, 5 grams.
III. ,, ,, at 235—250°, 43 grams.

The residue in the distilling flask solidified on cooling, and was found to be tribromotoluene; it crystallised from spirit in needles melting at 112—113°, properties which agree with Nevile and Winther's description of the tribromotoluene of the formula



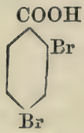
the melting point as stated by them being 111·2—112·8° (this Journal, 1880, 447).

0·3257 gram of the substance yielded on analysis 0·5565 gram silver bromide.

	Calculated for $C_6H_2MeBr_3$.	Found.
Br..........	72·94 per cent.	72·71 per cent.

With the exception of parabromotoluene, this was the only solid bromination product of toluene which I obtained, and I think it probable that Fittig's "dibromotoluene" melting at 107—108° was really this same tribromo-derivative, perhaps not quite pure. Its high melting point cannot otherwise be explained, as the constitution of the six possible dibromotoluenes is established (Nevile and Winther, Trans., 1880, **37**, 451), and none of these exhibit properties in agreement with Fittig's description. Of the tribromotoluenes, the one described above is the only one bearing any resemblance to Fittig's product.

The fraction 235—250° having been oxidised by dilute nitric acid, the resulting mixture of dibromobenzoic acids was examined as before. Theoretically, two, and only two, isomeric dibromobenzoic acids could be present, namely,



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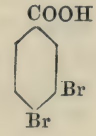


.

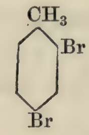
Each of these was, in fact, isolated. The acid obtained in larger quantity was found to be that of the formula [COOH : Br : Br = 1 : 3 : 4]. It melted at 232°; its barium salt crystallised with 4 mols. H_2O :—

0·2803 gram of salt lost 0·0264 gram water at 150°, and yielded 0·0854 gram BaSO$_7$.

	Calculated for $(C_6H_3Br_2{\cdot}COO)_2Ba,4H_2O$.	Found.
H_2O	9·39 p. c.	9·42 p. c.
Ba (in anhydrous salt)	19·71 ,,	19·80 ,,

The isomeride [COOH : Br : Br = 1 : 2 : 4] was also obtained in considerable quantity; it crystallised in needles melting at 169°, and its properties were, in fact, identical with those of the main oxidation product of the dibromotoluene from orthobromotoluene.

Parabromotoluene is thus shown to give rise to two dibromotoluenes on bromination, namely,



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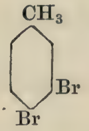
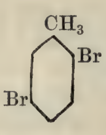
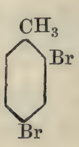


,

the latter of which appears to be produced in the larger proportion. The products from orthobromotoluene were as already stated,

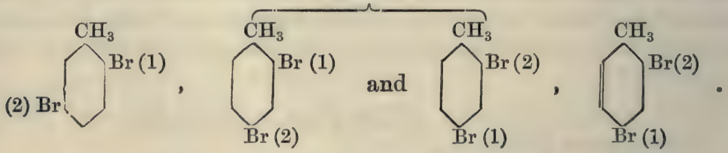


(chief product) and

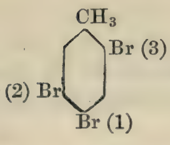


The latter of these being a product of the bromination of both ortho- and para-bromotoluene, three different isomeric dibromotoluenes may be said to result, under the conditions indicated, from the bromination of ortho- and para-bromotoluene, and hence from that of toluene itself.

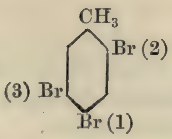
Whether the same result would be arrived at by the direct treatment of toluene with 2 molecular proportions of bromine I have not been able to ascertain, my experiments having been brought to an end through my leaving London. The results I have recorded do, however, indicate the different stages in the formation of the three dibromotoluenes and also of the tribromo-derivative obtainable from toluene. This is shown in the following symbols, in which the numbers indicate the order in which bromine atoms have entered the nucleus:—



In the case of the tribromotoluene which was obtained from parabromotoluene, either of the two following symbols might be taken to represent the stages of its formation, namely,



or



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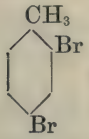
The first of these must, however, be considered the correct one. The second symbol represents the tribromotoluene to be derived from , and inasmuch as the latter is a product of the bromination of both ortho- and para-bromotoluene, it is to be expected that the tribromo-derivative would be obtained from both ortho- and para-bromotoluene, but this was not found to be the case. Assuming the first symbol to be correct, the formation of the tribromo-derivative from parabromotoluene, and its non-formation from orthobromotoluene, is at once explained.

A point of some interest in connection with the above experiments is brought out on comparing the results with those obtained by Seelig in the course of experiments on the chlorination of toluene (*Annalen*, **237**, 129—181). The conditions of chlorination which Seelig adopted certainly differed from those which I have described as adopted in my experiments on the bromination of toluene, but the differences between the chlorination and bromination products is more striking, I consider, than would have been expected. Seelig found, for instance, that orthochlorotoluene yielded as main product 1 : 2 : 3-dichlorotoluene together with a smaller proportion of the 1 : 2 : 4 isomeride, whereas parachlorotoluene yielded solely 1 : 2 : 4-dichlorotoluene.*

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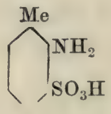
* Dr. Wynne, approaching the question from a different point of view, is also led (see footnote, p. 1051) to think that Seelig's conclusions are remarkable. He therefore proposes to re-examine the products obtained on chlorinating orthochlorotoluene.—H. E. A.

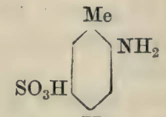
LXXXVII.—*Note on the Constitution of Nevile and Winther's Orthotoluidinesulphonic Acid and of the Sulphonic Acids of Orthochloro- and Ortho-bromotoluene.*

By W. PALMER WYNNE, D.Sc..

NEVILE and Winther (Trans., 1880, **37**, 626) found that when orthotoluidine hydrogen sulphate is heated at 220—230°, or on a sand-bath with constant stirring until the fused mass becomes solid, a single orthotoluidinesulphonic acid is produced; they ascertained that this acid contains its sulphonic radicle in the meta-position relatively to the methyl group, and it has therefore a constitution represented by one of the two formulæ



I.



II.

Numerous experiments were made with the object of deciding between the formulæ, and although no entirely satisfactory conclusion was arrived at, an examination of the products obtained by the action of bromine on the acid seemed to show that it has, in all probability, the constitution represented by the second symbol—a view which has met general acceptance.

Claus and Immel (*Annalen*, **265**, 67), after verifying the statements of Nevile and Winther with reference to the action of bromine on the acid,* found that the orthotoluidinesulphonic acid is convertible into an orthocresolsulphonic acid identical with that obtained by Claus and Jackson (*J. pr. Chem.* [2], **38**, 330) by the sulphonation of orthocresol. As the constitution [Me : OH : SO_3H = 1 : 2 : 5] assigned by Claus and Jackson to their acid was arrived at by analogy only and not by any direct proof, the problem still lacks the experimental evidence necessary for its complete solution.

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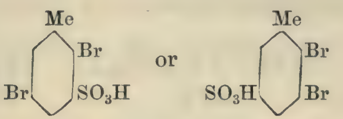
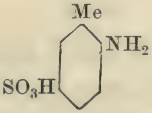
* It is noteworthy that on p. 70 of their paper, Claus and Immel make the following statement: "Durch Erhitzen mit Salzsäure im geschlossenen Rohr auf 120° bis 130° wird die o-Brom-o-toluidin-p-sulfonsäure, wie schon Neville und Winther angegeben haben, leicht entsulfonirt, indem das o-Brom-o-toluidin das in bei 56° (uncorr.) schmelzenden Nadeln Krystallisirt, entsteht." A reference to Nevile and Winther's paper shows that 1 : 2 : 3-bromorthotoluidine [Me : NH_2 : Br = 1 : 2 : 3] is a *liquid* (*loc. cit.*, p. 630; *Ber.*, **13**, 1945), that 1 : 2 : 5-bromorthotoluidine melts at 55—56° (*loc. cit.*, pp. 31, 435; *Ber.*, **13**, 963, 965), and that a mixture of dibromorthotoluidine (m. p. 43—44°), 1 : 2 : 5-bromorthotoluidine, and 1 : 2 : 3-bromorthotoluidine results from the hydrolysis with hydrochloric acid at 160°.

To ascertain the constitution of Nevile and Winther's acid, the following method has been employed. The metabromorthotoluidinemetasulphonic acid, obtained as described by these chemists by the careful bromination of the amido-acid, was converted by Sandmeyer's method into the corresponding dibromotoluenemetasulphonic acid,



On eliminating the sulphonic radicle, this afforded dibromotoluene, presenting all the characters of 1 : 2 : 3-dibromotoluene, whence it follows that Nevile and Winther's orthotoluidinemetasulphonic acid has the constitution commonly assigned to it,



The orthochlorotoluenesulphonic acid (compare following paper, p. 1072) and orthobromotoluenesulphonic acid (compare Nevile and Winther, *loc. cit.*, p. 628; Miller, preceding paper, p. 1023), obtained respectively from orthochlorotoluene and orthobromotoluene by sulphonation, also contain the sulphonic radicle in the meta-position relatively to the methyl group. As these acids were found to be identical with the corresponding products obtained by Sandmeyer's method from Nevile and Winther's acid, it follows that they likewise are 1 : 2 : 5-derivatives.

Experimental Part.

Orthotoluidinemetasulphonic acid was prepared from orthotoluidine hydrogen sulphate by Nevile and Winther's method, and purified by crystallisation of its sodium salt. The acid crystallised in needles with 1 mol. H_2O, and the sodium salt in elongated scales with 4 mols. H_2O, facts in agreement with the published description.

Metabromorthotoluidinemetasulphonic acid was prepared by slowly adding the calculated quantity of bromine in aqueous solution to a cold 2 per cent. aqueous solution of the acid. It crystallised from the concentrated solution in lustrous needles with 1 mol. H_2O, and the barium salt in long, lustrous needles with 3 mols. H_2O, as described by Claus and Immel. The *potassium* salt, $C_6H_2Me(NH_2)Br{\cdot}SO_3K$, crystallised in anhydrous, thin, lustrous scales, easily soluble in water, and the *sodium* salt, $C_6H_2Me(NH_2)Br{\cdot}SO_3Na + 18H_2O$, crystallised from a syrupy solution in small, apparently rectangular prisms, which, on exposure to the air, rapidly effloresced with the loss of all but a half molecular proportion of the water of crystallisation.

I. 0·4578 gram of the potassium salt lost 0·0002 gram at 175°, and gave 0·1296 gram K_2SO_4.

	Calculated for $C_6H_2Me(NH_2)Br{\cdot}SO_3K$.	Found.
K	12·83	12·70

II. 2·6322 grams of the crystallised sodium salt, after rapidly drying by pressure between filter paper, lost 1·3896 grams at 175°.

	Calculated for $C_6H_2Me(NH_2){\cdot}BrSO_3Na + 18H_2O$.	Found.
H_2O	52·94	52·79

III. 0·4258 gram of the effloresced sodium salt lost 0·013 gram at 175°, and gave 0·101 gram Na_2SO_4.

	Calculated for $C_6H_2Me(NH_2)Br{\cdot}SO_3Na + \frac{1}{2}H_2O$.	Found.
H_2O	3·03	3·05
Na (in dry salt)...	8·00	7·92

To further characterise the metabromorthotoluidinesulphonic acid, it was treated with excess of bromine in aqueous solution. The resulting dibromorthotoluidine, after distillation with steam and crystallisation from alcohol, was found to melt at 50°, as stated by Claus and Immel, and not at 45—46° as given by Nevile and Winther.

Orthometadibromotoluenemetasulphonic Acid.

To obtain this acid, 225 grams of the metabromamido-acid in a finely divided condition were suspended in water containing rather more than the calculated quantity of hydrogen bromide, diazotised with 20 per cent. sodium nitrite solution, and slowly added to a cold solution of cuprous bromide in hydrobromic acid. A vigorous evolution of gas at once took place. After removal of the copper salt by means of hydrogen sulphide, an almost theoretical yield of clean sodium dibromotoluenesulphonate was obtained by evaporation.

Barium dibromotoluenesulphonate, $(C_6H_2MeBr_2{\cdot}SO_3)_2Ba + 3\frac{1}{2}H_2O$, crystallised in thin, long needles, and dissolved sparingly in hot water.

0·425 gram of substance lost 0·0306 gram at 195°, and gave 0·116 ram $BaSO_4$.

	Calculated for $(C_6H_2MeBr_2{\cdot}SO_3)_2Ba + 3\frac{1}{2}H_2O$.	Found.
H_2O	7·34	7·20
Ba (in dry salt) ..	17·21	17·28

Potassium dibromotoluenesulphonate, $C_6H_2MeBr_2{\cdot}SO_3K$, crystallised in lustrous, long needles which were tolerably soluble in hot water.

0·4436 gram of substance lost 0·0008 gram at 195°, and gave 0·107 gram K_2SO_4.

	Calculated for $C_6H_2MeBr_2{\cdot}SO_3K$.	Found.
K	10·60	10·83

Sodium dibromotoluenesulphonate, $C_6H_2MeBr_2{\cdot}SO_3Na + H_2O$, crystallised in tufts of thin, long, flat needles, and was tolerably soluble in hot water.

0·4198 gram of the salt lost 0·0206 gram at 190°, and gave 0·0802 gram Na_2SO_4.

	Calculated for $C_6H_2MeBr_2{\cdot}SO_3Na + H_2O$.	Found.
H_2O	4·86	4·91
Na (in dry salt)...	6·53	6·50

Dibromotoluenesulphonic chloride, $C_6H_2MeBr_2{\cdot}SO_2Cl$, crystallised from light petroleum (b. p. 80°) or benzene in small, four-sided prisms, and from alcohol in radiate groups of needles. It melted at 93°.

0·2361 gram of substance gave, by the Carius method, 0·3517 gram of mixed AgCl and AgBr.

	Calculated for $C_6H_2MeBr_2{\cdot}SO_2Cl$.	Found.
Cl,Br	56·09	56·06

Dibromotoluenesulphonic bromide, $C_6H_2MeBr_2{\cdot}SO_2Br$, crystallised from light petroleum (b. p. 80°), in which it was somewhat sparingly soluble, in radiate groups of needles, and melted at 97°.

0·2579 gram of substance gave, by the Carius method, 0·3707 gram AgBr.

	Calculated for $C_6H_2MeBr_2{\cdot}SO_2Br$.	Found.
Br	61·07	61·17

The *sulphonamide*, obtained by heating either the chloride or the bromide with alcohol and ammonia, crystallised in small, sparingly soluble prisms, and melted at 214°.

To determine the orientation of the bromine in this acid, 100 grams of the sodium salt were heated with 400 grams of syrupy phosphoric acid, and hydrolysed by superheated steam. The operation was attended with much frothing, and was completed in the course of two hours. The product was distilled with steam, and amounted to 59 grams of crystalline dibromotoluene (87 per cent. of the theoretical) and 5 grams of an oil which did not completely crystallise on standing, and was not further examined. The dibromotoluene fused readily under warm water, and, on cooling, crystallised in large, flat prisms of a glassy lustre. It melted at 30—31°, instead of at 27·4—27·8° as given by Nevile and Winther.

0·2717 gram of substance gave, by the Carius method, 0·4086 gram AgBr.

	Calculated for $C_6H_3MeBr_2$.	Found.
Br	64·00	63·99

The nitro-derivative, obtained by treating this dibromotoluene with nitric acid (sp. gr. 1·500), crystallised from alcohol, in which it was sparingly soluble, in short, pale yellow needles which matted together by gentle pressure, and melted at 59°.

These properties are sufficient to identify this dibromotoluene with the 1 : 2 : 3-derivative (compare Nevile and Winther, *loc. cit.*, 434, 435), and to prove that Nevile and Winther's metabromorthotoluidinemetasulphonic acid has the constitution [Me : NH_2 : Br : SO_3H = 1 : 2 : 3 : 5], and their orthotoluidinemetasulphonic acid the constitution [Me : NH_2 : SO_3H = 1 : 2 : 5].

1 : 2 : 5-*Orthochlorotoluenesulphonic Acid.*

This acid was prepared by diazotising finely divided orthotoluidinesulphonic acid suspended in water containing the requisite amount of hydrogen chloride with 20 per cent. sodium nitrite solution, and stirring the product into a cold solution of cuprous chloride. After the vigorous action was complete, the copper was removed by means of hydrogen sulphide. On evaporating the filtrate, sodium orthochlorotoluenesulphonate was obtained in long, striated prisms associated with a half molecular proportion of water.

1 : 2 : 5-Orthochlorotoluenesulphonic chloride, $C_6H_3MeCl \cdot SO_2Cl$ crystallised from light petroleum (b. p. 80°) in elongated prisms of pearly lustre, and from benzene, in which it was easily soluble, in elongated, flat prisms, and melted at 65°.* Mr. W. J. Pope states that the crystals are crystallographically identical with those of the chloride obtained from the sulphonation product of orthochlorotoluene.

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* This melting point is about 5° higher than that previously recorded (*cf.* following paper, p. 1074).

0·2315 gram of substance gave, by the Carius method, 0·2953 gram AgCl.

	Calculated for $C_6H_3MeCl{\cdot}SO_2Cl$.	Found.
Cl	31·55	31·56

1 : 2 : 5-*Orthochlorotoluenesulphonic bromide*, $C_6H_3MeCl{\cdot}SO_2Br$, crystallised from light petroleum in elongated prisms, and from benzene, in which it was readily soluble, in thin, flat prisms. It melted at 67·5°.

0·2493 gram of substance gave, by the Carius method, 0·3067 gram of mixed AgCl and AgBr.

	Calculated for $C_6H_3MeCl{\cdot}SO_2Br$.	Found.
Cl,Br	42·87	42·86

The sulphonamide, prepared either from the chloride or the bromide, crystallised from dilute alcohol in thin, glistening scales, and melted at 128°.

1 : 2 : 5-*Orthobromotoluenesulphonic Acid.*

This acid was prepared from orthotoluidinesulphonic acid by the method already described under dibromotoluenesulphonic acid. The conversion of the diazo-compound by means of cold cuprous bromide solution left nothing to be desired, and the sodium salt obtained, after precipitating the copper with hydrogen sulphide and concentrating the filtrate, crystallised in colourless, striated prisms with $\frac{1}{2}$ mol. H_2O. The barium salt crystallised with 2 mols. H_2O.

1 : 2 : 5-Orthobromotoluenesulphonic chloride, $C_6H_3MeBr{\cdot}SO_2Cl$, crystallised from light petroleum in elongated prisms very similar in appearance to those of orthochlorotoluenesulphonic acid, and from benzene, in which it was easily soluble, in elongated, flat prisms. It melted at 61°.*

0·2428 gram of substance gave, by the Carius method, 0·2991 gram of mixed AgCl and AgBr.

	Calculated for $C_6H_3MeBr{\cdot}SO_2Cl$.	Found.
Cl,Br	42·87	42·92

1 : 2 : 5-Orthobromotoluenesulphonic bromide, $C_6H_3MeBr{\cdot}SO_2Br$, crystallised from light petroleum in small, glistening scales, and melted at 63·5°.*

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* This melting point is about 5° higher than that previously recorded (*cf.* following paper, p. 1074).

0·2378 gram of substance gave, by the Carius method, 0·2845 gram AgBr.

	Calculated for $C_6H_3MeBr{\cdot}SO_2Br$.	Found.
Br	50·96	50·91

The sulphonamide, prepared either from the chloride or the bromide, crystallised from dilute alcohol in long, slender needles, and melted at 147°.

The sulphonic chlorides and bromides described in this paper are being examined by Mr. W. J. Pope with the object of determining their crystallographical relationships. The halogen determinations in these compounds were made by Mr. R. L. Jenks, to whom the author's thanks are due for the assistance.

LXXXVIII.—*Action of Sulphuryl Chloride on Acetorthotoluidide and Acetoparatoluidide. Mono-, Di-, and Tri-chlorotoluenesulphonic Acids.**

By W. PALMER WYNNE, D.Sc.

THE first investigation of the behaviour of sulphuryl chloride with benzenoid derivatives was made by Dubois in 1866, who found that benzene and phenol were converted by its action, not into the expected sulphonic chlorides, but into chlorobenzene and chlorophenol respectively, with the evolution of sulphur dioxide and hydrogen chloride (*Zeit. für Chem.* [2], **2**, 705). Subsequent examination of the action of the chloride on aniline and acetanilide (Wenghöffer, *J. pr. Chem.* [2], **16**, 449), phenol (Gordon, *Proc. Chem. Soc.*, 1891, 64), resorcinol (Reinhard, *J. pr. Chem.* [2], **17**, 322), naphthalene (Armstrong, *Proc. Chem. Soc.*, 1891, 61), and β-naphthol (Armstrong and Rossiter, *Proc. Chem. Soc.*, 1889, 72; 1891, 32) has only served to confirm the conclusion arrived at by Dubois, that in its reactions with aromatic compounds sulphuryl chloride suffers decomposition into its generators, sulphur dioxide and chlorine, the latter then effecting substitution in the normal way.

The work embodied in this paper was the outcome of an investigation undertaken with the object of preparing 1 : 3 : 4-metaparadichlorotoluene in considerable quantity for use in the synthesis of the 1 : 2 : 1′- and 2 : 3 : 1′-dichlor-α-naphthols which Professor Armstrong and the author were desirous of examining in connection with their investigation of the tri-derivatives of naphthalene. This substance, according to Seelig, does not occur among the chlorination products of toluene (*Annalen*, **237**, 168), and has always been obtained from 1 : 3 : 4-metachloroparamidotoluene by the diazo-reaction.

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* From the thesis submitted in May, 1892, for the D.Sc. degree of the University of London.

Metachloroparatoluidine was first prepared by Wroblewsky from paratoluidine by chlorination of its acetyl derivative suspended in ice-cold water, and subsequent elimination of the acetyl radicle (*Annalen*, **168**, 196). The product, however, was not isolated in the pure state (*cf.* Lellmann and Klotz, *Annalen*, **231**, 310), and the method was therefore altered by Lellmann and Klotz, chlorine being passed through an ice-cold solution of acetoparatoluidide in six times its weight of acetic acid, but even under these improved conditions accompanied by the observance of special precautions, metachloracetoparatoluidide was only obtained "mit wechselndem Erfolg und in äusserst schlechter Ausbeute" (*loc. cit.*). The only other mode of preparation of metachloroparatoluidine on record at the time the present work was commenced (November, 1890) involved the chlorination of a solution of paratoluidine hydrochloride in 15 times its weight of 40 per cent. hydrochloric acid (Hafner, *Ber.*, **22**, 2536).

The difficulty to be overcome in the preparation of metachloroparatoluidine by these methods was apparently the tendency of the action of chlorine to proceed further with the production of dichloroparatoluidine on the one hand and of much resinous matter on the other.* It seemed probable that sulphuryl chloride might prove a more convenient chlorinating agent than chlorine for this purpose, because in the case of β-naphthol, the only recorded instance of a difference in the extent or nature of the action of these two chlorinating agents, it had been found that sulphuryl chloride gave the less complex product, the action of one molecular proportion of the chloride ending in the (quantitative) formation of 1 : 2-chloro-β-naphthol (Armstrong and Rossiter, *loc. cit.*) instead of proceeding further, as in the case of chlorine (Zincke and Kegel, *Ber.*, **21**, 3384), with the production of additive keto-compounds.

Preliminary experiments with the chloride soon made it clear that the resulting product was certainly not less complex than that obtained by the use of chlorine. On the other hand, however, a good yield of chlorinated base was obtained, and as the method of preparation was a convenient one in many respects, it was employed in the chlorination of 5 kilos. of acetoparatoluidide. In dealing with large quantities of material in this way, it became of interest to examine the secondary products of the action of sulphuryl chloride on acetoparatoluidide with the object of comparing them with those known to be formed by the action of chlorine on that substance. Further, in view of the complex nature of the product from the para-compound, it seemed desirable to examine the action of the chloride on the ortho-derivative, since acetorthotoluidide was not known to give more than one chloro-derivative on treatment with chlorine.

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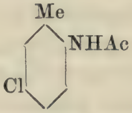
* This difficulty, so far as the production of higher chlorinated derivatives is concerned, has recently been successfully met by Lellmann, who has obtained a 40—42 per cent. yield of pure chloroparatoluidine by passing chlorine diluted with twice its volume of carbon dioxide through an ice-cold solution of acetoparatoluidide in eight times its weight of acetic acid (*Ber.*, **24**, 4111).

The chlorination was conducted by suspending the finely-powdered acetyl derivative in carbon bisulphide and gradually adding the sulphuryl chloride. After the reaction was ended and the carbon bisulphide removed by distillation, the product was hydrolysed with concentrated hydrochloric acid, and the base liberated from the resulting hydrochloride by means of sodium carbonate. The product from acetorthotoluidide was easily purified by fractional distillation. An attempt was also made to separate the various products from acetoparatoluidide by fractional distillation, but as no satisfactory result seemed likely to ensue, and as 1 : 3 : 4-dichlorotoluene was required for other purposes, it was abandoned and the products identified by substituting chlorine for the NH_2 radicle by Sandmeyer's method, and separating the corresponding chlorotoluenes partly by fractional distillation and partly by fractional sulphonation.

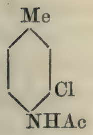
The results arrived at in the course of the work indicate a very close correspondence between the action of sulphuryl chloride and of chlorine on each of the acetylated bases, both in the extent to which substitution proceeds and in the relative positions assumed by the halogen in the molecule.

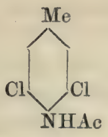
Acetorthotoluidide, on chlorination with a molecular proportion of sulphuryl chloride, is almost exclusively converted into

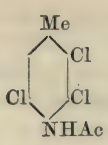


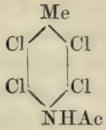
the proportion of higher chlorinated derivatives being extremely small. The result of the action of a molecular proportion of chlorine, according to Lellmann and Klotz (*Annalen*, **231**, 317) is the formation of the same 1 : 2 : 5-chloracetorthotoluidide as sole product.

Acetoparatoluidide, on the other hand, when chlorinated by means of a molecular proportion of sulphuryl chloride, yields a complex product in which the following chloro-derivatives seem to be present, although only the first two have actually been identified by means of their derivatives :—









The result of the action of a molecular proportion of chlorine on acetoparatoluidide in an ice-cold acetic acid solution is the formation of the same mono- and di-chloracetoparatoluidide* (Lellmann and Klotz, *loc. cit.*). With both chlorinating agents, 1 : 3 : 4-chloracetoparatoluidide is the chief product, the higher chlorinated derivatives being formed only in relatively small proportion.

The remarkable difference in the extent to which chlorination by means of sulphuryl chloride proceeds in the two cases is, no doubt, to be attributed largely to the fact that while chloracetorthotoluidide, like the two acetotoluidides, is practically insoluble in carbon bisulphide, chloracetoparatoluidide is dissolved to a considerable extent, and the chloride, therefore, in the later stages of the reaction, has the choice of acting either on the insoluble acetoparatoluidide or on the dissolved monochloro-derivative.

In the course of the examination of the sulphonation products of the mixed chlorotoluenes, it became necessary to prepare ortho- and para-chlorotoluenesulphonic acids for the purposes of comparison, and the opportunity was also taken to sulphonate metachlorotoluene. The results arrived at in the case of parachlorotoluenesulphonic acid are not in complete accordance with those obtained by Vogt and Henninger (*Annales de Chim. et Phys.* [4], **27**, 130), and by Hübner and Majert (*Ber.*, **6**, 791), agreeing better with those of the former chemists. The examination of these sulphonic acids is being continued with a view of determining their structure, since it is noteworthy that 1 : 2- and 1 : 3-chloro-, 1 : 2 : 5- and 1 : 3 : 4- dichloro-, and 1 : 3 : 4 : 5-trichloro-toluene seem each to give only one sulphonic acid on sulphonation, 1 : 4-chlorotoluene yielding a mixture of two containing the 1 : 3 : 4-parachlorotoluenemetasulphonic acid as chief product.

I. ACTION OF SULPHURYL CHLORIDE ON ACETORTHOTOLUIDIDE.

Acetorthotoluidide was prepared by boiling 750 grams of orthotoluidine with 1000 grams of glacial acetic acid for 13 hours, stirring the product into water, and afterwards crystallising from alcohol.

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* By passing a rapid stream of chlorine through a boiling solution of acetoparatoluidide in its own weight of acetic acid, Erdmann obtained the 1 : 3 : 4-chloro-derivative as chief product, together with a dichlorotoluidine which was not examined (*Ber.*, **24**, 2768).

The yield of pure acetyl derivative melting at 107° was found to be 757 grams.

The chlorination was carried out in the following way:—The finely powdered acetorthotoluidide (150 grams) was suspended in five times its weight of dry carbon bisulphide, and 150 grams of sulphuryl chloride slowly added in the cold, with frequent shaking, from a stoppered funnel. The flask was attached to a long reflux condenser connected with the draught to provide for the escape of the sulphur dioxide and hydrogen chloride evolved in the reaction. A smaller proportion of carbon bisulphide, 450 grams, was employed in the first experiment, but as loss of the chloride took place owing to the vigorous nature of the reaction, the quantity was increased to 750 grams in the later operations. The addition of the sulphuryl chloride was usually completed in an hour, and as soon as the action in the cold became slight, the flask was gradually warmed in a water-bath to the boiling point of the carbon bisulphide and kept at that temperature until all action ceased. The product, instead of dissolving in the bisulphide like that obtained from acetoparatoluidide, collected in small lumps at an early stage of the reaction, and some of the acetorthotoluidide no doubt escaped chlorination from this cause. After removal of the carbon bisulphide by distillation, chloracetorthotoluidide was left as a dry, granular mass in the flask.

The product was hydrolysed by heating the contents of the flask with 400 grams of hot hydrochloric acid (sp. gr. 1·16) in a water-bath. After a short time, a uniform solution was obtained which on further heating for about 15 minutes began to deposit crystals, and was, therefore, at once poured into a beaker and left to crystallise. The hydrochloride separated as a mass of beautiful, highly lustrous, thin plates, sparingly soluble in hydrochloric acid or water. After filtration and washing, it was converted into the base by suspending it, in quantities of about 50 grams, in hot water in a reflux apparatus and adding aqueous sodium carbonate from time to time until effervescence ceased and the liquid became permanently alkaline.

The base obtained in this way from 750 grams of acetorthotoluidide was purified by distillation with steam, the operation requiring very nearly 18 hours for its completion. During the first seven hours 195 grams of the base came over as an oil, which solidified under water in the course of three days at the summer temperature, while during the next eight hours the distillate, weighing 162 grams, solidified in the lower end of the condenser tube, and solidified at once under cold water. The remainder of the product, weighing 34 grams, then distilled over as an oil, which did not solidify in the course of 10 weeks, leaving a small amount of a brown, finely-divided residue in the distillation flask.

These distillates, after drying, were fractionally distilled. The first portion, weighing 195 grams, began to boil at 245°* under 753 mm. pressure, the temperature rising to 246°, while 4 drops passed over, at which point it remained constant, the last few drops passing over at 246·5°. The distillate, on standing for a short time, crystallised in a solid, white mass of small, thin plates, melting at 29·5—30°. The second portion, weighing 162 grams, gave a like result, almost the whole boiling at 246° under 746 mm. pressure. The distillate at first crystallised slowly in long, thin plates, but after a while the portion still remaining liquid crystallised rapidly in a white mass of small, thin plates similar to those of the first portion. It was not possible to separate the two forms of crystals, but the whole melted at 29·5—30°, and was shown to be identical with the first portion not only by the similarity in melting and boiling points, but also by conversion into the same acetyl derivative, into the same dichlorotoluene by Sandmeyer's method, and into the same chlorotoluene by elimination of the NH_2 radicle. The two portions were, therefore, united; the yield of pure chlororthotoluidine obtained in this way amounting to 50·1 per cent. of the theoretical.

The last portion of the steam distillate, weighing 34 grams, began to boil at 246° under 750 mm. pressure, and the temperature steadily rose to 254° during the distillation. Fractionation of the material was not attempted.

The acetyl derivative, prepared by the action of acetic chloride on the pure base, crystallised from dilute alcohol as a white, granular mass composed of tufts of small, slender needles, and melted at 139° (*cf.* Lellmann and Klotz, *Annalen*, **231**, 317).

Conversion of the Chlororthotoluidine into Chlorotoluene.

The method employed for the elimination of the NH_2 radicle was the hydrazine method of von Baeyer (*cf.* Haller, *Ber.*, **18**, 90), which had been found to give good results with substituted amidonaphthalenes (*cf.*, *inter alia*, Armstrong and Wynne, *Proc. Chem. Soc.*, 1889, 48; 1890, 11, 15, 16, 125, 126, 127, 128; 1891, 27), and was to be preferred in view of the known tendency of some chlorotoluidines to yield ethoxy-derivatives when diazotised and decomposed with absolute alcohol by Griess' method (*cf.* Wroblewsky, *Annalen*, **168**, 209; *Ber.*, **17**, 2703).

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* The boiling point determinations given in this paper were made with a Geissler's short distillation thermometer. The mercury thread was in every case completely immersed in the vapour, but no measures were adopted to screen the thermometer from the effects of radiation. As registered by this thermometer, water boiled at 100°, nitrobenzene at 209·7°, and quinoline at 237°, under 760 mm. pressure.

In the preliminary experiments undertaken to settle the identity of the two portions of the chlororthotoluidine, 25 grams of the base were used, but in the preparation of metachlorotoluene from this source for the purpose of sulphonation this quantity was doubled. A cream of the hydrochloride was prepared by stirring 50 grams of the fused base into a mixture of 80 grams of hydrochloric acid (sp. gr. 1·16) and 50 grams of water at 60°, and afterwards breaking down any crystalline lumps in a mortar. This was diazotised with the requisite quantity of a 20 per cent. potassium nitrite solution in an ice-bath, and the diazo-compound reduced by the addition of an ice-cold solution of 156 grams of stannous chloride in 420 grams of hydrochloric acid. During the reduction the mixture was kept carefully cooled in a freezing mixture of ice and salt, and the temperature maintained below 10°. The hydrazine salt separated at once in small, white scales sparingly soluble in dilute hydrochloric acid. After standing for 12 hours, the product was filtered, washed with dilute hydrochloric acid, then with water, suspended in a slight excess of a 2 per cent. copper sulphate solution, and the whole gradually heated to the boiling point in a reflux apparatus. Gas began to be given off at about 50°, and when the evolution ceased, the product was distilled with steam, washed with alkali, again distilled with steam, and dried. The amounts of unfractionated chlorotoluene obtained in two experiments with 25 grams of base were 9·5 and 12 grams, and in two experiments with 50 grams of base were 28 and 31 grams.

The 9·5- and 12-gram products were separately distilled to obtain the fractions boiling at 161—165° for the purposes of oxidation. The residues boiling above 165° from both sources weighed 9·5 grams, and were systematically fractionated with the 28- and 31-gram products under 750 mm. pressure with the following result:—

B. p. 160—165°	60 grams.
„ 165—190°	3 „
„ 190—200°	2 „
„ above 200°	3 „

Although the hydrochloride, possibly as tin double salt, was employed instead of the hydrazine, very fair yields were obtained, and the product evidently contained very little dichlorotoluene. This result is noteworthy, as hydrazines on oxidation either with cupric chloride (Armstrong and Wynne, *Proc. Chem. Soc.*, 1889, 48) or with a mixture of copper sulphate and hydrochloric acid (Gattermann and Hölzle, *Ber.*, **25**, 1074) are known to give derivatives in which the hydrazine radicle is replaced by chlorine instead of hydrogen.

That this product was metachlorotoluene was shown by heating it in quantities of about 3 grams with dilute nitric acid [4 vols. of nitric acid (sp. gr. 1·42) with 9 vols. of water] in sealed tubes at 130—140° for 8 hours. The resulting chlorobenzoic acid was freed from the small amount of nitro-acid formed in the reaction by steam distillation from a hydrochloric acid solution of stannous chloride, and on crystallisation from dilute alcohol was obtained in radiate groups of needles which melted at 152°.

Conversion of the Chlororthotoluidine into Dichlorotoluene.

The method employed was the modification of Sandmeyer's process described in connection with the preparation of orthochlorotoluene from orthotoluidine (p. 1072). Preliminary experiments with the first two portions of the steam distillate were made with 25-gram quantities, but in the preparation of the dichlorotoluene on the large scale 140 grams of the chlororthotoluidine were used in one operation, and the proportion of cuprous chloride doubled. To obtain the hydrochloride in a finely-divided condition, 350 c.c. of hydrochloric acid (sp. gr. 1·16) were rapidly added, with vigorous stirring, to 140 grams of the base suspended in 750 c.c. of water at 60°. In this form the reaction with 20 per cent. potassium nitrite solution in an ice-bath was a rapid one. The solution of the diazo-compound was gradually stirred into the requisite quantity of cold cuprous chloride solution prepared as described on p. 1059. Reaction ensued at once with the separation of a thick, reddish oil and evolution of nitrogen. The oil was separated next day, distilled with steam, washed with aqueous caustic soda, again distilled with steam, and dried. The amounts of unfractionated dichlorotoluene obtained in the two experiments with 25 grams of base were 16 and 18 grams; the yield in the third experiment with 140 grams of base was 142 grams, or 87·6 per cent. of the theoretical. On distillation under 765 mm. pressure, the last-named product was divided into the fractions—

B. p. 196—199°	37 grams.
,, 199°	84 ,,
,, 199—200°	16 ,,
,, above 200°	5 ,,

The identity of this product with the 1 : 2 : 5-dichlorotoluene prepared by Lellmann and Klotz (*Annalen*, **231**, 318) was established by oxidation. When heated with dilute nitric acid at 130—140° for 10 hours, it was almost completely oxidised to the corresponding dichlorobenzoic acid. After removal of the small quantity of dichlorotoluene by distillation with steam from an alkaline solution, the oxidation product was freed from accompanying nitro-acid by steam distillation from a hydrochloric acid solution of stannous chloride, and crystallised from dilute alcohol, from which it separated in a white mass made up of very small, almost microscopic, needles melting at 152°.

The 34 grams of oil forming the last portion of the steam distillate of the base gave a well-crystallised hydrochloride when stirred into 60 grams of hydrochloric acid diluted with 300 grams of hot water. It diazotised readily, and the resulting solution, when stirred into cold cuprous chloride solution, reacted at once with the evolution of nitrogen and formation of a viscid, red oil. This was purified by distillation with steam and treatment with alkali in the usual way, and when dried weighed 27 grams. On distillation under 765 mm pressure, it gave the following fractions:—

B. p. 199—208°	22·5 grams.
„ 208—210°	4 drops.
„ above 210°	4 grams.

Further fractionation was not attempted, as this result indicated the presence of only a small proportion of trichlorotoluene.

Sulphonation of 1 : 2 : 5-*Dichlorotoluene.*

In order to characterise 1 : 2 : 5-dichlorotoluene by other means than oxidation, and in order, also, to obtain a specimen of constant boiling point, it was decided to sulphonate the whole of the material without further fractionation. A trial experiment showed that 10 per cent. anhydrosulphuric acid was a convenient sulphonating agent. 185 grams of the dichlorotoluene, made up of 158 grams from pure chlororthotoluidine and 27 grams obtained from the liquid base, were shaken with 370 grams of the acid, and the action carried as far as seemed possible at 60—70°, the temperature attained during the first vigorous shaking of the materials. The unsulphonated portion, weighing 89 grams, was again shaken with 370 grams of the acid, and the action completed in a bath of boiling water. On cooling, the sulphonic acid crystallised in beautiful, thin plates, rendering the whole mass semi-solid, but went into solution in the excess of sulphuric acid on again heating in the water-bath. When poured into water the product dissolved, forming a slightly opalescent solution, which, on distillation with steam, gave less than half a gram of a thick, orange-red oil, which was not further examined. The clear solution was diluted with a large volume of hot water, neutralised with barium carbonate, and filtered hot. The residue was stirred into boiling water, again filtered, and finally extracted with aqueous potassium carbonate to remove any barium salt sparingly soluble in hot water. The united filtrates of the barium salt gave a large separation in scaly forms on cooling, and the mother liquor, on concentration, gave three more separations of similar appearance. The fifth separation (Ba in salt dried at 180°, 22·65 per cent.) consisted of small, crystalline particles, looking very much like eroded sand grains, and the sixth of small, white, spherical aggregates mixed with a few long, flat, narrow needles; both separations were small in amount.

Barium 1 : 2 : 5-*dichlorotoluenesulphonate*, $(C_6H_2MeCl_2{\cdot}SO_3)_2Ba + H_2O$.*—The first four separations of the barium salt were recrystallised, and required a considerable amount of water for their dissolution. The recrystallised salts were similar in appearance, consisting of small, thin plates of irregular shape, which, under a lens, were seen to be a mixture of very small, diamond-shaped plates with larger prismatic needles. All attempts to separate these forms, or to get the salt to crystallise in one form, were fruitless. When dry, the crystals had a mica-like lustre. On analysis, three successive separations gave the following figures:—

I. 0·3508 gram of substance lost 0·0094 gram at 210°, and gave 0·1294 gram $BaSO_4$.

II. 0·3432 gram of substance lost 0·0088 gram at 210°, and gave 0·1268 gram $BaSO_4$.

III. 0·3626 gram of substance lost 0·0098 gram at 210°, and gave 0·133 gram $BaSO_4$.

	Calculated for $(C_6H_2MeCl_2{\cdot}SO_3)_2Ba + H_2O$.	Found.		
		I.	II.	III.
H_2O	2·83	2·68	2·56	2·70
Ba (in dry salt) ..	22·19	22·28	22·28	22·15

Potassium 1 : 2 : 5-*dichlorotoluenesulphonate*, $C_6H_2MeCl_2{\cdot}SO_3K$.—This salt crystallised in radiate groups of long needles, which, on filtration, or when allowed to remain in the mother liquor, broke down into a crystalline powder. It was easily soluble in water, and, on analysis,

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* To judge from the description, the barium $(+H_2O)$ and sodium $(+H_2O)$ salts of the *α*-dichlorotoluenesulphonic acid obtained by Seelig in separating the "*α*-" and 1 : 2 : 4-dichlorotoluenes formed by the chlorination of orthochlorotoluene in the presence of ferric chloride are not improbably identical with those of 1 : 2 : 5-dichlorotoluenesulphonic acid (*Annalen*, **237**, 159). Seelig's *α*-dichlorotoluene, on oxidation, gave a dichlorobenzoic acid melting at 166° (*loc. cit.*, 168), but apart from this fact the arguments adduced in support of the constitution [Me : Cl : Cl = 1 : 2 : 3] assigned to the compound (*loc. cit.*, 181) would seem to apply equally to the constitution [Me : Cl : Cl = 1 : 2 : 5]. As the latter is the more probable on theoretical grounds, the author is engaged in a re-examination of the products formed on chlorinating orthochlorotoluene.

0·3928 gram of substance lost 0·0006 gram at 220°, and gave 0·1228 gram K_2SO_4.

	Calculated for $C_6H_2MeCl_2·SO_3K$.	Found.
K (in dry salt)	13·99	14·04

The salt obtained by extracting the barium sulphate residue with aqueous potassium carbonate, crystallised from the alkaline solution, and also from water, in small tufts of anhydrous needles (K in salt dried at 180°, 14·01 per cent.). The mother liquor, on concentration, gave a further separation in the form of small scales, consisting of a mixture of di- with some tri-chlorotoluenesulphonate (H_2O 4·07 per cent.; K in salt dried at 180°, 13·72 per cent.). This weighed 2·3 grams and was not further examined.

Sodium 1 : 2 : 5-*dichlorotoluenesulphonate*, $C_6H_2MeCl_2·SO_3Na + 1\frac{1}{2}H_2O$.—This salt crystallised in beautiful, long, slender needles, and was more soluble in water than the potassium salt. Two successive crystallisations were analysed:—

I. 0·3876 gram of substance lost 0·0364 gram at 215°, and gave 0·0952 gram Na_2SO_4.

II. 0·3704 gram of substance lost 0·035 gram at 215°, and gave 0·0914 gram Na_2SO_4.

	Calculated for	Found.	
	$C_6H_2MeCl_2·SO_3Na + 1\frac{1}{2}H_2O$.	I.	II.
H_2O	9·32	9·39	9·45
Na (in dry salt)	8·75	8·78	8·83

Finally, the sixth separation of the barium salt, which was found to contain some sodium salt, owing, no doubt, to the presence of a small quantity of sodium carbonate in the barium carbonate employed in neutralisation, was, together with the fifth separation, converted into sodium salt. Two salts, one crystallising in needles identical with the preceding, and the second in slender, colourless, nacreous scales, were separated by fractional crystallisation, and the latter, on analysis, proved to be sodium (ortho)chlorotoluenesulphonate, $C_6H_3MeCl·SO_3Na + H_2O$—

0·38 gram of substance lost 0·0286 gram at 220°, and gave 0·1084 gram Na_2SO_4.

	Calculated for $C_6H_3MeCl·SO_3Na + H_2O$.	Found.
H_2O	7·30	7·53
Na (in dry salt)....	10·07	10·00

1 : 2 : 5-*Dichlorotoluenesulphonic chloride*, $C_6H_2MeCl_2·SO_2Cl$, crystal-

lised from light petroleum (b. p. 50°), in which it was very soluble, in very large, probably anorthic, tables of brownish colour, and melted at 43°. The faces of the crystals were much corroded.

0·241 gram of substance gave, by the Carius method, 0·3985 gram AgCl.

	Calculated for $C_6H_2MeCl_2{\cdot}SO_2Cl$.	Found.
Cl	41·04	40·91

The *sulphonamide* crystallised from dilute alcohol in long, thin, flat needles, and melted at 191°.

1 : 2 : 5-Dichlorotoluene was obtained in a state of purity by the hydrolysis of pure potassium 1 : 2 : 5-dichlorotoluenesulphonate. Three hydrolyses were made, and in each 40 grams of the potassium salt were heated with 15 grams of water and 200 grams of strong sulphuric acid, and decomposed by superheated steam. Hydrolysis took place at once with very little frothing, and the operation was completed in the course of an hour. From the 120 grams of salt, 65·8 grams of dry dichlorotoluene were obtained, the yield amounting to 95·1 per cent. of the theoretical. This product, on the first distillation, gave 60·2 grams boiling at 200° under 770 mm. pressure, and the remainder at 200—201°. Pure 1 : 2 : 5-dichlorotoluene is, as described by Lellmann and Klotz (*loc. cit.*), a colourless, refractive liquid of pleasant odour.

II. Action of Sulphuryl Chloride on Acetoparatoluidide.

Acetoparatoluidide was prepared by boiling paratoluidine in 750-gram quantities with 1000 grams of glacial acetic acid for 12—13 hours, stirring the product into water, filtering, and crystallising from alcohol. The yield of pure acetyl derivative (m. p. 147°) in every case amounted to about the weight of paratoluidine taken.

After several trial experiments with quantities of sulphuryl chloride in excess of the theoretical proportion, it was found that about equal weights of acetoparatoluidide and sulphuryl chloride gave the best results, and these proportions were therefore adopted. The apparatus employed in the chlorination was that described in connection with acetorthotoluidide. In each operation, 140 grams of very finely powdered acetoparatoluidide were suspended in 700 grams of dry carbon bisulphide, and treated with 140 grams of sulphuryl chloride (an excess of 14 grams over the molecular proportion). Reaction started in the cold, and it was necessary to add the sulphuryl chloride slowly to prevent the action from becoming too vigorous, with a consequent loss of the volatile chloride. After the addition was completed and reaction had almost ceased in the cold—a stage reached usually in about two hours from the commencement—the flask was very gradually warmed in a water-bath to the boiling point of the carbon bisulphide, and kept at that temperature until the greater part of the material had gone into solution, and it was judged that all action had ceased, this part of the operation requiring about three hours for its completion. The carbon bisulphide was then removed by distillation from a water-bath, which towards the end of the process was heated to the boiling point. At this temperature the contents of the flask fused to a uniform viscid liquid, which, when allowed to cool, crystallised in small radiate groups of very thin scales.

To convert the product into the hydrochloride 300 grams of hot hydrochloric acid (sp. gr. = 1·16) were added to the hot viscid substance, a reflux condenser attached to the flask, and the heating in a bath of boiling water continued. After a short time the two layers mixed to a uniform liquid, which, after further heating for about 12 minutes, began to deposit crystals. The contents of the flask were then at once poured into a beaker and left to crystallise, a large separation in groups of thin plates, very sparingly soluble in hot or cold hydrochloric acid or in water, being obtained. This was filtered off next day. During the filtration through a linen cloth on the pump it was always found that a small quantity of a dark-brown oil collected in the pump flask, and the crystalline hydrochloride was freed as completely as possible from this by washing with small quantities of hydrochloric acid and of water, and by prolonged draining by the pump. The acid liquors separated from the oil were mixed with about six times their volume of water, which precipitated a considerable amount of a yellowish-white, flocculent substance. As the filtrate from this precipitate seemed to contain no other base than paratoluidine, and that only in small quantity, it was not further examined.

The crystalline hydrochloride was decomposed in quantities of about 50 grams by boiling with aqueous sodium carbonate in a reflux apparatus, the carbonate being added from time to time until no further effervescence was produced, and the liquid became permanently alkaline. The dark-brown oil so obtained was distilled with steam. At first a light-coloured oil, having a slight basic odour, passed over rapidly; but after some hours the rate began gradually to diminish, and the product to solidify in the receiver, and the process was stopped when the distillate commenced to solidify in the tube of the condenser. The base, after separation from the accompanying water, was dried over fused calcium chloride, and fractionated once with the following results:—

No. of operations	10*	10	17	Total.
	grams.	grams.	grams.	grams.
Acetoparatoluidide employed	1220	1400	2380	5000
Sulphuryl chloride "	1310	1400	2380	5090
Yield of base	604	680	1437	2721
B. p. 226—231°	403	510	924	1837
" 231—236°	98	107	271	476
" 236—250°	69	37	147	253
" above 250°	34	26	95	155

The dark-brown oil accompanying the crystalline hydrochloride, and the yellowish-white, flocculent precipitate obtained from the acid filtrate were boiled with aqueous sodium carbonate, but only gave a small quantity of base when distilled with steam. Like the residue left in the distilling flasks after removal of the 2721 grams of base by steam distillation, these products seem to consist of acetylated bases which had escaped hydrolysis during the first digestion with hydrochloric acid. The whole of this material was therefore boiled with a large excess of hydrochloric acid (sp. gr. = 1·16) in a reflux apparatus for about eight hours, and the product stirred into a large volume of water. A dark oily separation, which went semi-solid in the cold, was thus obtained. This was boiled with aqueous sodium carbonate, and the slightly alkaline mixture distilled with steam, the first portions of the distillate coming over as an oil which solidified on standing, the later portions solidifying in the tube of the condenser. A relatively small quantity of a black, brittle, resinous solid remained in the distilling flask, and as this was not affected by prolonged digestion with hot hydrochloric acid, it was not further examined.

The yield of the base recovered in this way amounted to 394 grams, and, on fractional distillation, the portion of the steam distillate which came over as an oil began to boil at 238°, while that which solidified in the condenser tube began to boil at 253°. The first portion was distilled separately until the temperature reached 250°, the second portion and the 155 grams boiling above 250° fractionated from the main product added, and the distillation continued up to 260°. Two fractions were thus obtained:—

B. p. 238—260°	248 grams.
" above 260°	301 "

As the high-boiling fraction in the distilling flask was dark in colour, and had a distinct odour of isonitrile, it was distilled with steam. The distillation was slow, particularly in its later stages, a small amount of dark-coloured residue remaining in the distilling flask. The distillate, weighing 294 grams, was collected in four portions:—

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* Six in the proportion of 140 grams of the base to 140 grams of the chloride.

1. Pale-yellow oil	80 grams.
2. Soft crystalline mass completely fused at 45°................	86 ,,
3. Hard crystalline mass melting at about 58°..................	65 ,,
4. Crystalline solid melting at about 64°..................	58 ,,

The dilute acid liquors, obtained by pouring the product of the eight hours' digestion with hydrochloric acid into water, were then rendered slightly alkaline with caustic soda, nearly 4 kilos. being required for the purpose. A dark-coloured oil began to separate just before the liquors became neutral in reaction, and the hot, slightly alkaline liquid on cooling deposited a mass of thin plates. The greater part of the supernatant liquid was siphoned off, and the residual matter, oil and crystals, distilled with steam. The recovered base seemed to distil over much more rapidly than the chloramidotoluene, and the pale-yellow, oily distillate, which towards the end of the operation came over only slowly, and solidified in the tube of the condenser, became semi-solid on standing, owing to the larger proportion crystallising in a mass of beautiful thin plates. The crystals were carefully drained from the remaining oil, and separately fractionated, but as the portion boiling above 218·5°, the temperature at which the oil began to boil, did not crystallise on cooling, the higher fractions were obtained from the mixed liquids. The base recovered from this source weighed 402 grams, and on fractionation gave the following results:—

B. p. 203—211° (a mass of colourless, slender plates in the cold)...................	193 grams.
,, 211—218·5° (semi-solid in the cold owing to a separation of plates in considerable quantity)........................	40 ,,
,, 218·5—224° (liquid when cold)........	57 ,,
,, 224—233° (,, ,,)........	47 ,,
,, above 233° (,, ,,)........	65 ,,

The preliminary fractionation showed that the product of the action of sulphuryl chloride contained not only the expected chloroparatoluidine, but also higher chlorinated derivatives, together with a corresponding amount of unattacked paratoluidine. A preliminary investigation, in which 7 grams of the fraction boiling at 226—231° were acetylated; 25 grams were diazotised and converted into dichlorotoluene by Sandmeyer's method, and 25 grams were converted into hydrazine, and oxidised with copper sulphate with the production of metachlorotoluene, showed that the chief product was the metachloroparatoluidine [Me : Cl : NH_2 = 1 : 3 : 4] of Lellmann and Klotz (*Annalen*, **231**, 310). An attempt was made to separate this base from the accompanying products by repeated fractionation, but as it seemed unlikely to lead to any satisfactory result, it was abandoned, and the various fractions converted into the corresponding chloro-derivatives by Sandmeyer's method, when 2757 grams of the base boiling below 260° had been collected in the following fractions (bar. 764 mm.) :—

B. p. 224—226°	328	grams.
,, 226—229°	1187	,,
,, 229—233°	732	,,
,, 233—238°	214	,,
,, 238—260°	248	,,
	2709	,,

The acetyl derivative, prepared by warming a portion of the base boiling at 226—231° with acetic anhydride, was crystallised from alcohol. It separated in beautiful, stellate groups of prismatic needles, or, by slow crystallisation, in large, flat prisms of glassy lustre, and melted at 113—113·5°.*

0·3236 gram of substance gave, by the Carius method, 0·249 gram AgCl.

	Calculated for $C_6H_3MeCl{\cdot}NHAc$.	Found.
Cl	19·30	19·03

Mr. W. J. Pope has had the kindness to measure the crystals, and reports as follows :—

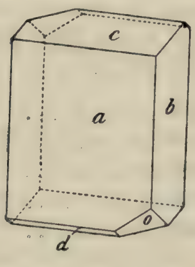
"This substance crystallises in beautiful, transparent, colourless tables of glassy lustre. The form *a*{100} is the largest on the crystals (next page), and is often striated parallel to the edges made by it with the other pinacoids *b* and *c*. There is a cleavage parallel to *a*{100}; the extinction through this form is approximately parallel to the pyramid edge. The dispersion is large. The forms $d\{101\}$ and $o\{111\}$ are frequently absent, and traces of the prism $\{110\}$ are sometimes seen.

---

* The melting point of this substance has been called in question by Erdmann, who found it to be 111—112° (*Ber.*, **24**, 2768), instead of 115°, as given by Lellmann and Klotz (*loc. cit.*). Lellmann has subsequently found the melting point of the substance to be 118° (*Ber.*, **24**, 4111), but in no case was a higher melting point than 113·5° attained with any of the specimens prepared in the course of this investigation.

" Forms present :—

a .... $\{100\}$ .... $\infty\bar{P}\infty$
b .... $\{010\}$ .... $\infty\breve{P}\infty$
c .... $\{001\}$ .... oP
d .... $\{101\}$ .... $'\bar{P}\infty'$
o .... $\{111\}$ .... $'P$



" Crystalline System. Anorthic.

$$a : b : c = 0·9391 : 1 : 0·6438.$$

$$\alpha = 90° 37'; \beta = 104° 43'; \gamma = 72° 6'.$$

	Angles.	Number of observations.	Limits.	Mean.	Calculated.
ab	100 : 010	24	71° 31′— 71° 45′	71° 38′	—
ab	100 : $0\bar{1}0$	17	108 15 —108 23	108 19	108° 22′
bc	010 : 001	21	94 3 — 94 26	94 12	—
bc	010 : $00\bar{1}$	13	85 35 — 85 53	85 50	85 48
ac	100 : 001	11	105 2 —105 38	105 21	105 17
ac	100 : $00\bar{1}$	19	74 39 — 74 51	74 43	—
bo	010 : 111	13	52 21 — 52 55	52 35	—
bo	$0\bar{1}0$: 111	2	127 11 —127 27	127 19	127 25
co	001 : 111	16	54 44 — 55 18	55 2	—
ad	100 : 101	3	64 40 — 66 21	65 33	64 39
cd	001 : 101	4	39 2 — 40 34	39 46	40 38
bd	010 : $\bar{1}0\bar{1}$	9	97 51 — 98 37	98 16	98 17
do	101 : 111	9	28 15 — 29 54	29 1	29 8
ao	100 : 111	5	59 10 — 61 4	60 3	60 5 "

Conversion of the Chloroparatoluidine b. p. 226—231° into Chlorotoluene.

The NH_2 radicle of the chloroparatoluidine was eliminated by the hydrazine method of von Baeyer. 25 grams of the base were converted into the hydrazine salt, and this oxidised with a 2 per cent.

copper sulphate solution exactly as described in connection with the preparation of metachlorotoluene from chlororthotoluidine (p. 1047). The yield amounted to 11 grams, of which 9 grams distilled at 162° under 776 mm. pressure.

The product was identified as metachlorotoluene, by heating it with dilute nitric acid at 130—140° for 10 hours. The resulting chlorobenzoic acid, after purification by the method already described, crystallised from dilute alcohol in radiate groups of long, slender needles, and melted at 152—153°.

Conversion of the Chloroparatoluidine b. p. 224—260° *into Dichlorotoluene.*

A preliminary experiment, with 25 grams of the base, showed that good results were obtained by the modification of Sandmeyer's method, described in connection with the preparation of orthochlorotoluene (p. 1072). The proportion of cuprous chloride, however, was doubled in the subsequent experiments, and a copper solution for each 100 grams of base was prepared by dissolving 60 grams of copper carbonate in 650 grams of hydrochloric acid (sp. gr. 1·16) diluted with 100 grams of water, and boiling the solution with copper turnings until colourless. The hydrochloride was formed by adding 250 c.c. of hydrochloric acid (sp. gr. 1·16), with rapid stirring, to 100 grams of the base suspended in 600 c.c. of water at 50°; a clear solution was momentarily obtained, but immediately afterwards the hydrochloride began to crystallise out, and was caused to separate in a finely-divided form by cooling rapidly and stirring vigorously. The hydrochloride, suspended in the dilute acid and cooled in an ice-bath, was diazotised with a 25 per cent. sodium nitrite solution. In the case of the fractions of the base boiling at 224—226° and 226—229°, a clear solution of the diazo-compound was always obtained, but, with the other fractions, some brown-coloured oil was formed during the reaction with the nitrite, and the amount of this, though small in the case of the fraction boiling at 229—233°, was larger with that boiling at 233—238°, and quite considerable with that boiling at 238—260°, making it difficult to ascertain the end of the reaction by starch-iodide paper. In none of these cases was any evolution of gas noticed during diazotisation, and, as the temperature was carefully kept below 5°, the formation of the oil can hardly have been due to decomposition of the diazo-compound.

The solution of the diazo-compound was gradually stirred into the cold cuprous chloride solution. In every case, very little gas was given off at first, but afterwards the reaction proceeded briskly with the evolution of nitrogen and separation of a reddish oil. After remaining in contact with the copper liquors during the night, the oily product was separated, distilled with steam, shaken with alkali, again distilled with steam, and dried. The amount of residue in the distillation flasks was very small, except in the case of the product from the fraction boiling at 238—260°.

The total amount of base employed was 3156 grams, and the yield of unfractionated chlorotoluenes amounted to 2467 grams.

This material was then systematically fractionated with the object of isolating as much 1 : 3 : 4-dichlorotoluene as possible, and as the result of a considerable number of operations, it was separated into the following fractions (bar. 763·5 mm.) :—

B. p. 160—165° (parachlorotoluene)	94 grams.
„ 205·5—206·5° (1 : 3 : 4-dichlorotoluene)	1501 „

together with—

B. p. 165—202°............	170 grams.
„ 202—209°............	273 „
„ above 209°	413 „

The uniformity of the parachlorotoluene and the dichlorotoluene separated in this way was established by sulphonation, and in view of the results obtained the remainder of the product was separated into its constituents by sulphonation instead of by further fractionation.

Sulphonation of 1 : 3 : 4-*Dichlorotoluene, b. p.* 205·5—206·5°.

In order to characterise the chlorotoluene boiling at 205·5—206·5°, and to obtain evidence as to its purity, 50 grams were converted into the corresponding sulphonic acid. Trial experiments showed that pure (100 per cent.) sulphuric acid took up very little of the product on shaking, that 5 per cent. anhydrosulphuric acid dissolved it completely on shaking, but took up very little of the material boiling above 209°, and that 10 per cent. anhydrosulphuric acid dissolved it readily, and also largely converted the material boiling above 209° into sulphonic acid. The dichlorotoluene was therefore shaken with three times its weight (150 grams) of 5 per cent. anhydrosulphuric acid until dissolved, the mixture becoming warm during the reaction. The product, on exposure to the (moist) air for some hours, crystallised from the excess of sulphuric acid in minute, slender needles. After dilution with water, it was converted into barium salt, which was fractionally crystallised and found to be uniform with the exception of the sixth separation of 1·43 grams, which crystallised from the last 80 c.c. of the mother liquor on concentration in less well-defined tufts of short, slender, white needles. These, on recrystallisation, gave numbers (Ba = 22·22 per cent., H_2O = 5·69 per cent.) indicating the composition $(C_6H_2MeCl_2{\cdot}SO_3)_2Ba + 2H_2O$. The corresponding potassium salt (K = 13·97 per cent.) crystallised in bundles of long, slender needles, very similar in appearance to the ordinary barium salt, except that they were semi-opaque and not white. The quantity of material was insufficient to admit of further examination.

Barium 1 : 3 : 4-*dichlorotoluenesulphonate*, $(C_6H_2MeCl_2{\cdot}SO_3)_2Ba$ + (?)$2H_2O$, crystallised from water, in which it was sparingly soluble, in bundles of beautiful, long, white, very slender needles aggregated together in tufts. Analyses of (I) the first and (II) the fifth separations were made—

I. 0·3272 gram of substance lost 0·0158 gram at 200°, and gave 0·1174 gram $BaSO_4$.

II. 0·337 gram of substance lost 0·0165 gram at 200°, and gave 0·1204 gram $BaSO_4$.

	Calculated for $(C_6H_2MeCl_2{\cdot}SO_3)_2Ba + 2H_2O$.	Found. I.	Found. II.
H_2O	5·52	4·83	4·89
Ba (in dry salt) ..	22·19	22·15	22·07

No further loss of weight occurred when these salts were heated at 240—250°.

Potassium 1 : 3 : 4-*dichlorotoluenesulphonate*. $C_6H_2MeCl_2{\cdot}SO_3K$, crystallised from water in thin, long, prismatic needles of calcite-like lustre, and was sparingly soluble in cold water. The salt obtained by extracting the barium sulphate residue with potassium carbonate, with the object of removing any sparingly soluble barium sulphonate, crystallised in forms identical with these. Analyses were made of the salt from (I) the crystallised barium salt, and (II) the barium sulphate residue.

I. 0·3822 gram of substance lost 0·0004 gram at 185°, and gave 0·1192 gram K_2SO_4.

II. 0·3906 gram of substance lost 0·0006 gram at 205°, and gave 0·122 gram K_2SO_4.

	Calculated for $C_6H_2MeCl_2{\cdot}SO_3K$.	Found. I.	Found. II.
K..........	13·99	14·00	14·02

Sodium 1 : 3 : 4-*dichlorotoluenesulphonate*, $C_6H_2MeCl_2{\cdot}SO_3Na$ + H_2O, crystallised from water, in which it was comparatively sparingly soluble, in beautiful, long, slender, brittle needles. On analysis, the following numbers were obtained :—

0·398 gram of substance lost 0·0262 gram at 200°, and gave 0·1002 gram Na_2SO_4.

	Calculated for $C_6H_2MeCl_2\cdot SO_3Na + H_2O$.	Found.
H_2O	6·41	6·58
Na (in dry salt)	8·75	8·73

1 : 3 : 4-*Dichlorotoluenesulphonic chloride*, $C_6H_2MeCl_2\cdot SO_2Cl$, crystallised from light petroleum, in which it was somewhat sparingly soluble, in splendid, long, monosymmetric prisms, having a calcite-like lustre. It melted at 82°.

0·2911 gram of substance gave, by the Carius method, 0·4827 gram AgCl.

	Calculated for $C_6H_2MeCl_2\cdot SO_2Cl$.	Found.
Cl	41·04	41·02

The *sulphonamide* crystallised from alcohol in sparingly soluble, well defined, elongated prisms, and melted at 189°.

Sulphonation of the Mixture of Chlorotoluenes accompanying 1 : 3 : 4-*Dichlorotoluene* (*b. p.* 205·5—206·5) *boiling above* 165°.

The various fractions of the product (p. 1060) were, in view of the experience gained in the sulphonation of parachlorotoluene (p. 1078) and 1 : 3 : 4-dichlorotoluene, systematically extracted, first with pure (100 per cent.) sulphuric acid, then with 5 per cent., and finally with 10 per cent. anhydrosulphuric acid. In every case the chlorotoluene was vigorously shaken with three times its weight of the acid, employed in two portions, until no further appreciable diminution of the upper layer took place, the mixture being heated in a water-bath at 70—80°, to assist the reaction. The product was then poured into water and distilled with steam. The oil after drying was fractionated, and the fractions, united with others of the same boiling point, were shaken with fresh quantities of acid of suitable strength. The sulphonic acids were united according as they were obtained by the use of pure sulphuric acid, or of 5 or 10 per cent. anhydrosulphuric acid, and then converted into barium salts in the usual way.

In the course of this fractional separation, 1120 grams of pure (100 per cent.) sulphuric acid, 1870 grams of 5 per cent., and 274 grams of 10 per cent. anhydrosulphuric acid were employed, and the 856 grams of the mixed chlorotoluenes were divided into—

195 grams dissolved by the pure sulphuric acid.
506 ,, ,, ,, 5 per cent. anhydro-acid.
123 ,, ,, ,, 10 per cent. ,,
31 ,, insoluble in 10 per cent. anhydrosulphuric acid under the conditions employed.

(*a.*) *Examination of the Sulphonic Acid obtained by the use of Pure Sulphuric Acid.*—The barium salt from this source was submitted to fractional crystallisation. The first three separations consisted of pure barium 1 : 3 : 4-dichlorotoluenesulphonate in the characteristic bundles of white needles; the fourth and fifth of a mixture of barium mono- and di-chlorotoluenesulphonates crystallising in white, branched clusters of small, sand-grain-like forms; the sixth, seventh, and eighth of barium parachlorotoluenesulphonate as a mixture of the powdery, microcrystalline form described on p. 1079 with scales; and the ninth and remaining separations of barium parachlorotoluenesulphonate in thin, lustrous, curved scales.

The separation of the mixed barium mono- and di-chlorotoluenesulphonates proved troublesome, but was accomplished by employing solutions of such a strength that crystallisation did not at once ensue when they became cold. Under these circumstances the dichloro-salt slowly separated in the characteristic form. On concentrating slightly and again cooling, a further crop of white tufts of slender needles was obtained, and by repeating the operation several times, a complete separation was achieved. The mother liquor then gave the aggregates of small, irregularly shaped, sand-grain-like crystals characteristic of the "A" form of parachlorotoluenesulphonic acid, and finally a mixture of the powdery, microcrystalline form mixed with scales, which, with their mother liquor, were united with the similar material of the sixth, seventh, and eighth separations.

The fractional crystallisation of this mixture of barium parachlorotoluenesulphonates was then undertaken, and found to be even more difficult than in the case of the separation of the corresponding material from pure parachlorotoluene. This was probably due to an interference with crystallisation caused by the presence of a small quantity of barium 1 : 3 : 4-dichlorotoluenesulphonate which could not be separated, but gave evidence of its presence by the uniformly low percentages of barium in the salts analysed. After many trials, resulting in the isolation of 17 grams of the sand-grain form, and only 5 grams of the scaly form, the attempt to separate this product into its constituents by fractional crystallisation was abandoned.

The salts isolated in the course of the work were:—

Barium 1 : 3 : 4-dichlorotoluenesulphonate........	156 grams.
,, parachlorotoluenesulphonate "A"........	35 ,,
,, ,, "B" (scales).	22 ,,

the remainder being barium parachlorotoluenesulphonate in the form of a mixture of the powdery, microcrystalline form with scales. The following analyses, selected from a number, may be quoted:—

I. Third (original) separation in needles: 0·4026 gram lost 0·0198 gram at 190°, and gave 0·145 gram $BaSO_4$.

II. Fourth (original) separation in white, branched clusters of sand grains: 0·388 gram lost 0·0112 gram at 185°, and gave 0·152 gram $BaSO_4$.

III. Needles separated from II: 0·3814 gram lost 0·0188 gram at 190°, and gave 0·139 gram $BaSO_4$.

IV. Sand grains separated from II: 0·3896 gram lost 0·0122 gram at 205°, and gave 0·1598 gram $BaSO_4$.

V. Sixth (original) separation in the powdery, microcrystalline form mixed with scales: 0·3708 gram lost 0·0108 gram at 195°, and gave 0·1498 gram $BaSO_4$.

VI. Sand grains separated from V: 0·4046 gram lost 0·012 gram at 195°, and gave 0·1640 gram $BaSO_4$.

VII. Scales separated from V: 0·3882 gram lost 0·0116 gram at 205°, and gave 0·1572 gram $BaSO_4$.

VIII. Ninth (original) separation in scales: 0·381 gram lost 0·0124 gram at 195°, and gave 0·1546 gram $BaSO_4$.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
H_2O	4·92	2·89	4·93	3·13	2·91	2·97	2·99	3·25
Ba (in dry salt)..	22 25	23·70	22·52	24·88	24·45	24·55	24·53	24·65

The "A" and "B" salts of parachlorotoluenesulphonic acid separated in this way were each converted into the corresponding potassium and sodium salts. These resembled in all respects the salts from pure parachlorotoluene described on pp. 1080 and 1081.

(*b.*) *Examination of the Sulphonic Acid obtained by the use of* 5 *per cent. Anhydrosulphuric Acid.*—The barium salt of this product was submitted to fractional crystallisation. The first 10 separations consisted of pure barium 1 : 3 : 4-dichlorotoluenesulphonate,* the 11th and 12th, weighing together 13 grams, of small, pale-brown, crystalline aggregates which decrepitated at 140°,† and four further separations, weighing together 16·8 grams, of lustrous scales. The crystalline aggregates were separated by crystallisation into barium 1 : 3 : 4-dichlorotoluenesulphonate and a salt crystallising in scales [H_2O = 2·58 per cent.; Ba (in dry salt) = 24·12 per cent.], which was mixed with the last separations. The total weight of barium 1 : 3 : 4-dichlorotoluenesulphonate from this source was 907 grams. The barium sulphate residue was extracted with aqueous potassium carbonate, and gave only 6·2 grams of the potassium salt (K = 13·93 per cent.).

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* No trace of the second form of this salt described on p. 1061 was discovered in this product.

† The difference between this salt and the intermediate salt (containing about the same percentage of barium) obtained from the 100 per cent. sulphuric acid product is noteworthy. It is perhaps to be accounted for by the fact that the

Analyses of the (I) 10th, (II) 11th, and (III) 12th separations, and (IV) of the barium dichlorotoluenesulphonate separated by fractional crystallisation of the mixed 11th and 12th separations are given:—

I. 0·3642 gram of substance lost 0·0180 gram at 205°, and gave 0·1308 gram $BaSO_4$.

II. 0·385 gram of substance lost 0·046 gram at 200°, and gave 0·1348 gram $BaSO_4$.

III. 0·3162 gram of substance lost 0·0404 gram at 200°, and gave 0·1104 gram $BaSO_4$.

IV. 0·3566 gram of substance lost 0·0176 gram at 190°, and gave 0·1286 gram $BaSO_4$.

	I.	II.	III.	IV.
H_2O	4·94	11·95	12·78	4·93
Ba (in dry salt)..	22·20	23·37	23·52	22·29

The salt crystallising in scales was found, after some examination, to consist largely of barium chloride, no doubt present as an impurity in the barium carbonate used for neutralisation. It was converted into sodium salt, and a small separation of sodium (para)chlorotoluenesulphonate, weighing 3·8 grams, in very soluble, slender needles [H_2O = 6·69 per cent.; Na (in dry salt) = 9·68 per cent.], was isolated from the accompanying sodium chloride.

The extraction of parachlorotoluene from the mixed chlorotoluenes by means of pure (100 per cent.) sulphuric acid was therefore very complete.

(*c.*) *Examination of the Sulphonic Acid obtained by the use of* 10 *per cent. Anhydrosulphuric Acid.*—The barium salt of this sulphonic acid was less soluble in water than the salts of the preceding products, and it was necessary to extract the barium sulphate residue several times with aqueous potassium carbonate.

The barium salt was fractionally crystallised, and five separations

former crystallised from solutions containing little else but barium chloride (H_2O in $BaCl_2,2H_2O$ = 14·75 per cent.), while the latter crystallised from solutions containing barium parachlorotoluenesulphonate (H_2O = 3·18 per cent.).

obtained: the first in small plates; the second in small, prismatic forms; the third in tufts of curved, flat needles; the fourth in white tufts of slender, white needles; and the fifth in small, white aggregates of minute needles. The first four separations were recrystallised from water, and eventually the product was found to consist of two salts only, barium trichlorotoluenesulphonate and barium 1 : 3 : 4-dichlorotoluenesulphonate. Although the former was distinctly less soluble in water than the latter, the separation of the two was not easy, and was only effected by dissolving the mixed salt in the minimum of water at 85°, watching the crystallisation, and filtering immediately any needles made their appearance among the diamond-shaped scales or flat, curved needles of the trichloro-derivative. Even under these conditions, the apparently uniform trichloro-salt (*cf.* analyses II and III) would frequently be found on analysis to give numbers indicating the presence of a considerable percentage of dichloro-derivative. Every separation of supposed trichloro-salt, and 14 were obtained, had therefore to be analysed. The following analyses may be quoted:—

I. First (original) separation: 0·373 gram lost 0·0098 gram at 210°, and gave 0·1256 gram $BaSO_4$.

II. Thin, flat, curved needles of irregular outline: 0·357 gram lost 0·009 gram at 210°, and gave 0·12 gram $BaSO_4$.

III. Separation, indistinguishable from II in appearance, from mother liquor of II: 0·3794 gram lost 0·0112 gram at 200°, and gave 0·1326 gram $BaSO_4$.

IV. Fourth (original) separation: 0·3546 gram lost 0·0168 gram at 200°, and gave 0·1258 gram $BaSO_4$.

	I.	II.	III.	IV.
H_2O	2·62	2·52	2·95	4·74
Ba (in dry salt)..	20·32	20·26	21·16	21·88

The amounts of the two salts isolated were—

Barium trichlorotoluenesulphonate	40·5 grams.
,, 1 : 3 : 4-dichlorotoluenesulphonate ..	81·0 ,,

The fifth separation of the barium salt, weighing 19 grams, was found to be a mixture of the barium and sodium* salts of 1 : 3 : 4-dichlorotoluenesulphonic acid. Mixed with its mother liquor, it was therefore converted into sodium salt, which crystallised in slender needles, and on analysis gave the numbers—

---

* Due no doubt to the presence of a small quantity of sodium carbonate in the barium carbonate used. This sample of barium carbonate was purchased subsequently to that containing small quantities of barium chloride (p. 1065), and from a different firm.

0·409 gram of substance lost 0·0258 gram at 200°, and gave 0·1038 gram Na_2SO_4.

	Calculated for $C_6H_2MeCl_2 \cdot SO_3Na + H_2O$.	Found.
H_2O	6·41	6·31
Na (in dry salt)..	8·75	8·77

The potassium salt, weighing 56 grams, obtained by extracting the barium sulphate residue with aqueous potassium carbonate, was likewise found to be a mixture of di- with tri-chlorotoluenesulphonate, the latter being present in the larger quantity. The first separation, weighing 19 grams, from the strongly alkaline solution consisted of scales, which crystallised from water in the same form; and the second, weighing 17 grams, of long, flat, radiate needles, unaltered by recrystallisation. It was not found possible to fractionally crystallise the salts remaining in the mother liquor either from the alkaline liquor or from water, but a separation was effected by crystallisation from 80 per cent. alcohol, as described in connection with potassium trichlorotoluenesulphonate (p. 1069). Analyses of (I) the first and (II) the second separations were made:—

I. 0·3536 gram of substance lost 0·0006 gram at 185°, and gave 0·097 gram K_2SO_4.

II. 0·364 gram of substance lost 0·025 gram at 185°, and gave 0·099 gram K_2SO_4.

	Calculated for $C_6HMeCl_3 \cdot SO_3K$.	Found.	
		I.	II.
H_2O	—	—	6·87
K (in dry salt) ..	12·45	12·32	13·09

The total amount of trichloro-salt separated from the mixed potassium salt was 33 grams.

The fractional separation of the chlorotoluenes, by means of sulphuric acid of the three strengths employed, was, therefore, fairly complete, as may be seen from the table (p. 1068), which gives the amounts of the chlorotoluenes equivalent to the weights of the various salts isolated in the course of the separation of the chlorotoluenesulphonic acids.

The loss of about 9 per cent. in the case of the product from the 5 per cent. anhydrosulphuric acid, and of about 10 per cent. in that from the 10 per cent. anhydrosulphuric acid, probably occurred during the large number of fractional crystallisations made in the course of the work. It is worthy of note, however, that Seelig experienced a loss of 9—28 per cent. in the course of a fractional separation of a mixture of ortho- and para-chlorotoluene by means of sulphuric acid (*Annalen*, **237**, 152).

Acid.	Parachlorotoluene.	1 : 3 : 4-Dichlorotoluene.	Trichlorotoluene.	Weight recovered.	Weight sulphonated.
Pure sulphuric	28*	78	—	106*	195
5 per cent. anhydro-	2	458	—	460	506
10 per cent. anhydro-	—	68	43	111	123
Total.....	30*	604	43	677*	824

As a result, therefore, of fractional distillation and fractional sulphonation, the following amounts of mono-, di-, and tri-chlorotoluene were separated from the 2467 grams of mixed chlorotoluenes, obtained by applying Sandmeyer's method to the chlorination product from 5 kilos. of acetoparatoluidide.

	Separated by		
	Distillation.	Sulphonation.	Total.
Parachlorotoluene	94	30†	124†
1 : 3 : 4-Dichlorotoluene....	1501	604	2105
Trichlorotoluene	—	43	43
Higher chlorinated toluenes	—	31	31

The yield of pure 1 : 3 : 4-dichlorotoluene, therefore, amounted to 39 per cent. of the theoretical.

Hydrolysis of 1 : 3 : 4-*Dichlorotoluenesulphonic Acid.*

The various amounts of barium 1 : 3 : 4-dichlorotoluenesulphonate isolated in the way just described were united and converted into potassium salt, which was partly used in the preparation of pure 1 : 3 : 4-dichlorotoluene. 11 hydrolyses were made, and in each 50 grams of the salt were heated with 20 grams of water and 250 grams of strong sulphuric acid and decomposed by superheated steam. Hydrolysis commenced at once, and the operation was usually completed in the course of an hour. The total yield of dichlorotoluene from 550 grams of salt amounted to 297 grams, or 93·5 per cent. of the theoretical, the yield in individual experiments varying from 90·1 per cent. to 95·9 per cent. of the theoretical. This product, on the first distillation, gave 291 grams boiling at 207° under 764 mm. pressure.

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* As stated on p. 1063, the separation of the parachlorotoluenesulphonic acid was not completed. The amount here given of 28 grams corresponds with the 57 grams of the two forms of the barium salt actually isolated. If an allowance is made for a probable 10 per cent. loss in the separation of the dichlorotoluenesulphonic acid, the parachlorotoluene in this fraction would, by difference, amount to 106 grams.

† See preceding note.

Pure 1 : 3 : 4-dichlorotoluene is, as described by Lellmann and Klotz (*loc. cit.*), a colourless, strongly-refractive liquid. The corresponding dichlorobenzoic acid, prepared by heating 5 grams of the pure material with 15 grams of phosphorus pentachloride at 190—200° (*cf.* Colson and Gautier, *Compt. rend.*, **101**, 1064; **102**, 1075), and oxidising the resulting benzal derivative with potassium permanganate in alkaline solution, crystallised from alcohol in long, slender, flat needles, and melted at 202°.

Examination of the Trichlorotoluenesulphonic Acid.

Barium trichlorotoluenesulphonate, $(C_6HMeCl_3 \cdot SO_3)_2Ba + H_2O$, crystallised from hot water, in which it was sparingly soluble, either in characteristic groups of four or five thin, curved, narrow, elongated scales, springing from a common point and having their flat faces superposed like a closed fan, or in distinct, thin, but not curved, elongated scales of irregular outline. On analysis, it gave the numbers—

0·3524 gram of substance lost 0·0084 gram at 200°, and gave 0·1176 gram $BaSO_4$.

	Calculated for $(C_6HMeCl_3 \cdot SO_3)_2Ba + H_2O$.	Found.
H_2O	2·52	2·38
Ba (in dry salt) ..	19·97	20·09

Potassium trichlorotoluenesulphonate, $C_6HMeCl_3 \cdot SO_3K$, crystallised from water in small scales, and was less soluble than the dichloro-salt. When dissolved in the minimum quantity of water at 80°, and treated with absolute alcohol (about five times the volume) in such quantity that crystallisation did not commence until the solution was very nearly cold, it crystallised in groups of long, slender, flat needles, and, when dry, had a brilliant lustre. As the dichloro-salt in a mixture of the two, like that described on p. 1067, did not separate from such a solution for some hours, and then came out in tufts of very slender needles, it was not difficult to isolate both in the pure state. Analyses of (I) the salt prepared from pure barium salt, (II) salt forming first crop of crystals from the mixture "II" analysed on p. 1067, and (III) salt forming second crop of crystals from the same are given :—

I. 0·3546 gram of substance lost 0·0006 gram at 210°, and gave 0·0984 gram K_2SO_4.

II. 0·3086 gram of substance lost 0·0006 gram at 205°, and gave 0·0854 gram K_2SO_4.

III. 0·3658 gram of substance lost 0·0124 gram at 210°, and gave 0·1096 gram K_2SO_4.

	Calculated for $C_6HMeCl_3{\cdot}SO_3K$.	Found.		
		I.	II.	III.
H_2O	—	—	—	3·39*
K (in dry salt) ..	12·45	12·46	12·43	13·90

Sodium trichlorotoluenesulphonate, $C_6HMeCl_3{\cdot}SO_3Na + \frac{1}{2}H_2O$, crystallised from 33 per cent. alcohol in white tufts of very slender needles, which were easily soluble in water.

0·3952 gram of substance lost 0·0122 gram at 205°, and gave 0·0954 gram Na_2SO_4.

	Calculated for $C_6HMeCl_3{\cdot}SO_3Na + \frac{1}{2}H_2O$.	Found.
H_2O	2·94	3·09
Na (in dry salt)..	7·74	8·07

Trichlorotoluenesulphonic chloride, $C_6HMeCl_3{\cdot}SO_2Cl$, crystallised from light petroleum (b. p. 50°), in which it was easily soluble, in short needles, and melted at 88°.

0·2164 gram of substance gave, by the Carius method, 0·4258 gram AgCl.

	Calculated for $C_6HMeCl_3{\cdot}SO_2Cl$.	Found.
Cl............	48·30	48·68.

1 : 3 : 4 : 5-*Trichlorotoluene* was obtained by the hydrolysis of a mixture of 21 grams of potassium trichlorotoluenesulphonate with 10 grams of water and 100 grams of concentrated sulphuric acid. The yield amounted to 12·6 grams, or 96 per cent. of the theoretical. During the distillation with steam the first 10 grams solidified in the condenser tube, but the remainder came over as an oil. Both products distilled completely at 245·5—247° under 768 mm. pressure, and the crystalline solid fused at 42·5°. On oxidation with dilute nitric acid at 170—180° for 10 hours, the same trichlorobenzoic acid was obtained both from the solid and the oil; and this, when purified from nitro-acid in the way already described, crystallised from dilute alcohol in slender needles melting at 202—203°. The oil solidified in an ice-bath, and fused again at the ordinary temperature, but the

---

* Although this salt crystallised with ½ mol. H_2O, and differed in appearance from the ordinary form of potassium 1 : 3 : 4-dichlorotoluenesulphonate, it gave the same dichlorotoluenesulphonic chloride melting at 81·5—82°.

small quantity separated from the oxidation product by steam distillation from an alkaline solution, like the corresponding material recovered from the solid, crystallised under water and fused at 43°. The difference between the melting points of these two portions of the otherwise apparently uniform trichlorotoluene remains to be accounted for.

The following analyses were made:—

I. 0·2084 gram of the trichlorotoluene gave, by the Carius method, after heating for 34 hours at 270°, 0·454 gram AgCl.

	Calculated for $C_6H_2MeCl_3$.	Found.
Cl............	54·47	53·89

II. 0·2278 gram of the trichlorobenzoic acid, dried at 100°, gave, by the Carius method, 0·4357 gram AgCl.

	Calculated for $C_6H_2Cl_3{\cdot}COOH$.	Found.
Cl............	47·23	47·31

Salkowski (*Annalen*, **163**, 28) and Claus and Bücher (*Ber*., **20** 1626) have described a trichlorobenzoic acid melting at 203°, which is believed to have the structure [$COOH : Cl_3 = 1 : 3 : 4 : 5$]. The known trichlorotoluenes, the 1 : 2 : 3 : 4- and the 1 : 2 : 4 : 5-derivatives, differ in properties from the above (Seelig, *Annalen*, **237**, 131), which must have the constitution assigned,* the alternative 1 : 2 : 4 : 6-formula being most improbable in view of the fact that the 1 : 3 : 4-derivative has been shown to be the only dichlorotoluene; and, therefore, the only chloracetoparatoluidide present in the product of the action of sulphuryl chloride on acetoparatoluidide.

Examination of the Chlorotoluene insoluble in 10 *per cent. Anhydrosulphuric Acid.*

The 31 grams of this material were distilled under a pressure of 771 mm., and gave the following fractions:—

B. p. 260—268°..........	1 gram.
,, 268—273°..........	4 grams.
,, 273—278°..........	8 ,,
,, 278—284°..........	9 ,,
,, 284—294°..........	3 ,,
,, above 294°..........	6 ,,

---

* The fact that Lellmann and Klotz (*loc. cit.*) obtained 1 : 3 : 4 : 5-dichloroparamidotoluene by the action of chlorine on 1 : 3 : 4-chloracetparatoluidine is an additional argument in favour of the constitution assigned to the new trichlorotoluene.

It would seem, therefore, to contain chiefly tetrachlorotoluene with some pentachlorotoluene. All the distillates were crystalline.

The examination of this high-boiling chlorotoluene, and also of the crystalline high-boiling chloroparamidotoluenes described on p. 1056, is being continued.

III. Sulphonation of the Isomeric Chlorotoluenes.

Orthochlorotoluenesulphonic Acid.

In one of the series of important papers dealing with the replacement of the diazo-radicle by halogens, Sandmeyer describes the preparation of orthochlorotoluene from orthotoluidine by a method involving the formation of orthodiazotoluene in a nearly boiling 10 per cent. solution of cuprous chloride, and states that the yield amounted to about 31 per cent. of the theoretical (*Ber.*, **17**, 2651). As this could not be regarded as a satisfactory yield, and as poor yields seemed to be obtained only when the process was employed with orthamido-derivatives, the use of cuprous chloride solution in the cold was suggested by Professor Armstrong, and found to give excellent results. Orthodiazotoluene chloride, obtained by dissolving 54 grams of orthotoluidine in a mixture of 135 grams of hydrochloric acid (sp. gr. 1·16) and 80 grams of water, cooling in an ice-bath, and adding the requisite amount of sodium nitrite in the form of a 25 per cent. solution, was stirred into an ice-cold solution of cuprous chloride, made by suspending 25 grams of cuprous chloride in 500 c.c. of water and adding sufficient hydrochloric acid for its dissolution. Reaction at once ensued with the evolution of nitrogen and formation of a red solid, which, on remaining in contact with the cuprous chloride solution at the ordinary temperature during the night, underwent change with the production of oily orthochlorotoluene. This was distilled with steam, washed with aqueous caustic soda, again distilled with steam, dried, and fractionated. Under these conditions yields of 50, 54, and 54 grams of orthochlorotoluene boiling at 156—157°, amounting to 84·6 per cent. of the theoretical in the last two cases, were obtained in three successive experiments with the quantities given. With a solution containing 10 grams instead of 25 grams of cuprous chloride, the yields obtained in two experiments with 54 grams of orthotoluidine amounted only to 28 and 30 grams, but the question whether this decrease was due exclusively to the reduction in the quantity of cuprous chloride employed cannot be regarded as settled until further experiments have been made.

Orthochlorotoluenesulphonic acid was prepared by shaking

75 grams of orthochlorotoluene with 225 grams of pure (100 per cent.) sulphuric acid; the mixture became very warm, and sulphonation was completed by warming in a water-bath at 60° for ten minutes. The acid, when poured into water, gave a clear solution, which was neutralised with barium carbonate, filtered, and fractionally crystallised in the way already described. Only one sulphonic acid seemed to be formed under the conditions employed, since the various separations of the barium salt were uniform with the exception of the last two, the sixth and seventh, which crystallised in minute scales, and together weighed only 2·4 grams. Hübner and Majert (*Ber.*, **6**, 791) likewise obtained only one orthochlorotoluenesulphonic acid by the action of fuming sulphuric acid on a mixture of ortho- and para-chlorotoluene, and although their acid is in all probability identical with the above, it is to be noted that the descriptions and the amounts of water of crystallisation of the salts of the two acids do not always agree.

Barium orthochlorotoluenesulphonate, $(C_6H_3MeCl{\cdot}SO_3)_2Ba + 2H_2O$, crystallised in lustrous, thin, long prisms, sparingly soluble in hot water. The crystals were occasionally sufficiently thin to be flexible. Analyses of the first and fourth separations were made:—

I. 0·4412 gram of substance lost 0·028 gram at 190°, and gave 0·176 gram $BaSO_4$.

II. 0·4232 gram of substance lost 0·0266 gram at 190°, and gave 0·169 gram $BaSO_4$.

	Calculated for $(C_6H_3MeCl{\cdot}SO_3)_2Ba + 2H_2O$.	Found. I.	Found. II.
H_2O	6·17	6·35	6·29
Ba (in dry salt)..	24·98	25·03	25·04

Potassium orthochlorotoluenesulphonate, $C_6H_3MeCl{\cdot}SO_3K + \frac{1}{2}H_2O$, crystallised from a comparatively dilute solution in beautiful, thin scales, which when dry had a satin-like lustre.

0·381 gram of substance lost 0·014 gram at 185°, and gave 0·13 gram K_2SO_4.

	Calculated for $C_6H_3MeCl{\cdot}SO_3K + \frac{1}{2}H_2O$.	Found.
H_2O	3·55	3·67
K (in dry salt)...	15·95	15·88

Sodium orthochlorotoluenesulphonate, $C_6H_3MeCl{\cdot}SO_3Na + \frac{1}{2}H_2O$, crystallised from dilute solutions in thin, finely striated, brittle plates, often more than a centimetre in length, and from concentrated solutions in narrower, but otherwise similar, forms. When dry, the salt had a calcite-like lustre. Analyses of two separations were made, as the water of crystallisation differed from that of the sodium chlorotoluenesulphonate isolated in the purification of 1 : 2 : 5-dichlorotoluene by sulphonation (p. 1052) :—

I. 0·3792 gram of substance lost 0·0152 gram at 185°, and gave 0·1134 gram Na_2SO_4.

II. 0·3774 gram of substance lost 0·0152 gram at 190°, and gave 0·1126 gram Na_2SO_4.

	Calculated for $C_6H_3MeCl{\cdot}SO_3Na + \frac{1}{2}H_2O$.	Found.	
		I.	II.
H_2O	3·79	4·01	4·03
Na (in dry salt)..	10·07	10·09	10·07

Orthochlorotoluenesulphonic chloride, $C_6H_3MeCl{\cdot}SO_2Cl$, crystallised from light petroleum (b. p. 50°), in which it was easily soluble, in long, flattened, irregularly developed prisms of pearly lustre, belonging to the anorthic system. It melted at 60°.

0·3222 gram of substance gave, by the Carius method, 0·4101 gram AgCl.

	Calculated for $C_6H_3MeCl{\cdot}SO_2Cl$.	Found.
Cl............	31·55	31·49

The *sulphonamide* crystallised from dilute alcohol in thin, glistening scales, and melted at 128°.

It was proved that this acid contained its sulphonic radicle in the meta-position relatively to the methyl group, as on reduction with sodium amalgam it gave toluenemetasulphonic acid, identified by its amide. An attempt was made to convert it into the corresponding dichlorotoluene by distilling the chloride with phosphorus pentachloride, and so to determine its constitution; but, as in the case of the distillation of orthobromotoluenesulphonic bromide with phosphorus pentabromide (Nevile and Winther, Trans., 1880, 629; Miller, this vol., p. 1030), the result was unsatisfactory. From 75 grams of the chloride, heated in quantities of 25 grams with the calculated quantity of phosphorus pentachloride at 190° for 10—15 minutes until the reaction seemed to be complete, 12 grams of an oil, having the irritating odour of benzyl compounds, and boiling between 207° and 240°, were obtained. The oil, on treatment with sulphuric acid at 60—70°, evolved hydrogen chloride, and the product when poured into water had an odour recalling that of benzaldehyde, indicating that substitution of chlorine for hydrogen in the methyl radicle occurred during the reaction with the pentachloride. The aqueous solution seemingly contained a dichlorotoluenesulphonic acid, sinc a barium salt (8·2 grams) was obtained from it which crystallised with four molecular proportions of water (H_2O, 10·48 per cent.; Ba, in the salt dried at 195°, 22·43 per cent.) in small, pale yellow, crystalline aggregates. This was not further examined, as it evidently differed from the barium salt of 1 : 2 : 5-dichlorotoluenesulphonic acid, and as the sulphonic acid obtained from orthochlorotoluene by sulphonation was in the meantime shown to be identical with that derived from Nevile and Winther's orthotoluidinesulphonic acid (compare preceding paper).

It is noteworthy that while the melting points of the amides agree, those of the chlorides of the acids obtained from the two sources differ by 5°; a like difference also occurs in the case of the orthobromotoluenesulphonic bromides (compare Miller, this vol., p. 1030; preceding paper, p. 1041). The cause of this difference has not yet been ascertained.

Metachlorotoluenesulphonic Acid.

The metachlorotoluene employed in the preparation of this acid was prepared from 1 : 2 : 5-metachlororthamidotoluene by elimination of the amido-group (p. 1048). The acid was obtained by shaking 60 grams of metachlorotoluene with 180 grams of pure (100 per cent.) sulphuric acid; the mixture became warm, and the reaction was completed by warming in a water-bath at 70° for a few minutes. The product dissolved completely in water, and was converted into barium salt by neutralisation with barium carbonate. The barium salt was then fractionally crystallised, and at first it seemed probable that two isomeric sulphonic acids had been formed in the reaction, since the first separation of the barium salt was found on recrystallisation to come out as a mixture of small, lustrous scales with irregularly shaped crystalline aggregates. The latter could be separated by elutriation, and, when recrystallised, came out in the same form; the potassium salt and the metachlorotoluenesulphonic chloride obtained from this form were identical with the corresponding compounds from the barium salt crystallising in scales. The barium salt must therefore be regarded as dimorphous.

Barium metachlorotoluenesulphonate, $(C_6H_3MeCl\cdot SO_3)_2Ba + H_2O$, usually crystallised in small, nacreous scales, smaller than, but otherwise similar in appearance to, the scaly form of barium parachlorotoluenesulphonate; it was, however, more soluble in hot water than the latter salt. It was also obtained in aggregates of small, irregular crystals, as just described. Analyses of the two forms were made.

I. 0·3584 gram of the aggregates lost 0·0118 gram at 210°, and gave 0·1474 gram of $BaSO_4$.

II. 0·3948 gram of the scales lost 0·0124 gram at 205°, and gave 0·1628 gram of $BaSO_4$.

	Calculated for $(C_6H_3MeCl{\cdot}SO_3)_2Ba + H_2O$.	Found.	
		Aggregates.	Scales.
H_2O	3·18	3·29	3·14
Ba (in dry salt) ..	24·98	25·00	25·02

Potassium metachlorotoluenesulphonate, $C_6H_3MeCl{\cdot}SO_3K$, crystallised in small, thin, almost square plates, showing well-defined edges. When dry, it had a vitreous lustre. Analyses of the salt prepared from the barium salt crystallising (I) in aggregates and (II) in scales were made; the former was dried in the air for five, and the latter for two days.

I. 0·3974 gram of substance lost 0·0024 gram at 210°, and gave 0·141 gram K_2SO_4.

II. 0·3984 gram of substance lost 0·0028 gram at 210°, and gave 0·1406 gram K_2SO_4.

	Calculated for $C_6H_3MeCl{\cdot}SO_3K$.	Found.	
		I.	II.
H_2O	—	0·60	0·70
K (in dry salt)...	15·95	16·00	15·93

Sodium metachlorotoluenesulphonate, $C_6H_3MeCl{\cdot}SO_3Na + H_2O$, crystallised from water in rhombs belonging to the monosymmetric system. The crystals had a pearly lustre, and usually showed striations parallel with the edges on the two largest faces, giving them the appearance of being intersected by two diagonals.

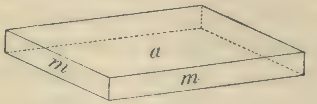
0·3946 gram of substance lost 0·0298 gram at 190°, and gave 0·1134 gram Na_2SO_4.

	Calculated for $C_6H_3MeCl{\cdot}SO_3Na + H_2O$.	Found.
H_2O............	7·30	7·55
Na (in dry salt)..	10·07	10·07

Mr. W. J. Pope, who is examining the sulphonic chlorides described in this paper, has had the kindness to measure the crystals of the potassium and sodium salts of this acid. He reports as follows:—

" *Potassium Metachlorotoluenesulphonate.*

" This compound crystallises in large, transparent rhombs having a vitreous lustre The pinacoïd *a* {100} is well developed, and sometimes striated parallel to its edges; the form *m*{011} is small, and generally also deeply corroded in lines parallel to its edges.



" Forms present:—

a .... {100} .... ∞P̶∞
m .... {011} .... P̸∞

" Crystalline System. Monosymmetric.

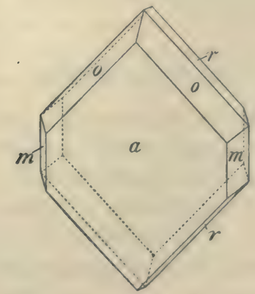
$$a : b : c = \ ? \ : 1 : 0{\cdot}8805.$$
$$\beta = 81^\circ\ 22'.$$

	Angles.	Number of observations.	Limits.	Mean.	Calculated.
am	100 : 011	7	83° 20′—83° 48′	83° 30′	—
am	1̄00 : 011	6	96 24 —96 36	96 31	96° 30′
mm	011 : 011̄	9	97 46 —98 6	97 59	97 55
mm	011 : 01̄1	12	82 4—82 6	82 5	—

" There is a good cleavage parallel to *a*{100} and an imperfect one parallel to *m*{011}.

" *Sodium Metachlorotoluenesulphonate.*

" This salt forms large, six-sided, transparent, colourless crystals of pearly lustre. With the exception of the pinacoïd {100}, all the forms are very small and frequently rounded. The form *a*{100} is generally striated on one face; an optic axis emerges in the plane of symmetry through this form. The dispersion is large. There is a poor cleavage parallel to *a*{100}. The forms *l*{011} and *s*{211̄} occur but seldom, and give very poor reflections.



“ Forms present :—

a	{100}	∞Ᵽ∞
m	{110}	∞P
o	{111}	−P
r	{11$\bar{1}$}	+P
s	{21$\bar{1}$}	2Ᵽ2
l	{011}	Ꝑ∞

“ Crystalline System. Monosymmetric.

$$a : b : c = 2{\cdot}0786 : 1 : 0{\cdot}8936.$$
$$\beta = 59° \, 8'.$$

	Angles.	Number of observations.	Limits.	Mean.	Calculated.
am	100 : 110	14	60° 12′—61° 15′	60° 44°	—
mm	110 : $\bar{1}$10	11	57 54—59 3	58 33	58° 32′
om	111 : 110	16	40 10—40 52	40 35	—
mr	110 : 11$\bar{1}$	3	56 20—57 9	56 41	57 1
ao	100 : 111	14	50 17—51 13	50 41	—
ar	100 : 11$\bar{1}$	4	93 54—94 12	94 2	94 8
or	111 : $\bar{1}$11	6	34 58—35 51	35 19	35 11
ol	111 : 011	3	15 2—15 34	15 18	15 18
rl	$\bar{1}$11 : 011	·5	19 32—20 19	19 59	19 53
as	100 : 21$\bar{1}$	3	72 51—73 33	73 9	73 16
os	111 : $\bar{2}$11	1	—	56 7	56 3”

Metachlorotoluenesulphonic chloride, $C_6H_3MeCl{\cdot}SO_2Cl$, crystallised from light petroleum (b. p. 50°), in which it was easily soluble at the boiling point, in brilliant, long, orthorhombic prisms melting at 53°.

0·2019 gram of substance gave, by the Carius method, 0·2579 gram AgCl.

	Calculated for $C_6H_3MeCl{\cdot}SO_2Cl$.	Found.
Cl............	31·55	31·60

The *sulphonamide* crystallised from dilute alcohol in very small, thin scales, and melted at 182°.

Parachlorotoluenesulphonic Acids.

The parachlorotoluene employed was a portion of that isolated in the course of the examination of the product obtained by the action of sulphuryl chloride on acetoparatoluidide; it boiled at 161—165°. The acid was prepared by shaking 50 grams of parachlorotoluene with 150 grams of pure (100 per cent.) sulphuric acid. About one half of the parachlorotoluene was readily taken up by the acid, the mixture becoming warm, but the remainder went up only slowly, even after warming in a water-bath, and sulphonation was only completed by heating the mixture in a bath of boiling water for 40 minutes, and shaking frequently. The product dissolved completely in water, and was converted into barium salt by neutralisation with barium carbonate. On fractional crystallisation, three separations were obtained: the first in aggregates of small, transparent, irregular crystals much resembling sand grains; the second, by evaporation of the mother liquor, in a finely divided, white, microcrystalline form; and the third in uniform, thin, nacreous scales.

The first separation was recrystallised from water, in which it was sparingly soluble. The crystalline form was unaltered, and a second similar separation was obtained by concentrating the mother liquor. From dilute alcohol the salt crystallised in uniform scales, closely resembling in appearance the more soluble barium salt, but these again crystallised in the sand-grain form from water. Two analyses of the salt were made: (I) the sand-grain form crystallised from water; (II) scales crystallised from dilute alcohol.

I. 0·442 gram of substance lost 0·013 gram at 220°, and gave 0·1814 gram $BaSO_4$.

II. 0·381 gram of substance lost 0·012 gram at 200°, and gave 0·156 gram $BaSO_4$.

	Calculated for $(C_6H_3MeCl{\cdot}SO_3)_2Ba + H_2O$.	Found.	
		I.	II.
H_2O	3·18	2·94	3·15
Ba (in dry salt)..	24·98	24·85	24·84

The intermediate salt was recrystallised from water, in which it was sparingly soluble. A first separation in aggregates of small, sand-grain-like crystals was obtained without difficulty, but much trouble was experienced in getting a uniform salt from the mother liquor, which constantly gave mixed separations of scales with the finely-divided, microcrystalline form. By elutriation of the mixed salt with warm water, a solution was eventually obtained, which gave uniform, thin, nacreous scales in three successive separations. The intermediate salt therefore seemed to be derived from a mixture of the acids yielding salts crystallising respectively in aggregates of small, irregular crystals and in scales, and the separation into its constituents of the portion remaining after removal of the scales by elutriation was not proceeded with. Analyses of the three kinds of barium salt obtained in the course of this fractional crystallisation were made: (I) sand grains; (II) white, microcrystalline form separated from scales by elutriation; (III) scales—

I. 0·3836 gram of substance lost 0·0114 gram at 195°, and gave 0·1576 gram $BaSO_4$.

II. 0·3820 gram of substance lost 0·0114 gram at 195°, and gave 0·1572 gram $BaSO_4$.

III. 0·3956 gram of substance lost 0·0114 gram at 195°, and gave 0·1632 gram $BaSO_4$.

	Calculated for $(C_6H_3MeCl{\cdot}SO_3)_2Ba + H_2O$.	Found.		
		I.	II.	III.
H_2O	3·18	2·97	2·98	2·88
Ba (in dry salt)..	24·98	24·88	24·93	24·96

A third separation of the barium salt, that in small, nacreous scales, was recrystallised from water, in which it was somewhat more soluble than the sand-grain form. From the warm solution it crystallised uniformly in very thin, curved scales, but as the solution cooled, at 30° or thereabouts, a second form consisting of aggregates of much smaller scales frequently made its appearance. Crystallisation from dilute alcohol led to a similar result. This second form could never be obtained free from the first, and as its appearance was found to be dependent on the temperature of the solution, uniform separations were got without much difficulty by filtering off the thin, curved scales from the warm solution, concentrating the filtrate, again filtering warm, and so on. Six separations were obtained in this way, and analyses were made of (I) the first, and (II) the sixth:—

I. 0·3856 gram of substance lost 0·0122 gram at 200°, and gave 0·1588 gram $BaSO_4$.

II. 0·3914 gram of substance lost 0·0132 gram at 200°, and gave 0·1618 gram $BaSO_4$.

	Calculated for $(C_6H_3MeCl{\cdot}SO_3)_2Ba + H_2O$.	Found.	
		I.	II.
H_2O	3·18	3·16	3·37
Ba (in dry salt)..	24·98	24·99	25·14

As a result, the following amounts of the barium salts were obtained:—

"A" salt crystallising in sand-grain-like forms..	34 grams.
"B" ,, ,, scales	38 ,,
Mixed ,, ,, microcrystalline aggregates remaining after a partial separation of the similar "intermediate" salt into the sand-grain and scaly forms	16 ,,

The barium salt "A" crystallising in sand-grain-like forms was converted into the potassium and sodium salts.

Potassium parachlorotoluenesulphonate, $C_6H_3MeCl{\cdot}SO_3K + \frac{1}{3}H_2O$, crystallised from an aqueous solution containing potassium carbonate in small quantity in bundles of silky looking, very slender needles, from water in very slender, long, radiate needles, and from 50 per cent. alcohol in long, slender, flat needles, which when dry showed a nacreous lustre. All the separations seemed uniform. The salt crystallised from dilute alcohol was analysed :—

0·4019 gram of substance lost 0·0098 gram at 190°, and gave 0·137 gram K_2SO_4.

	Calculated for $C_6H_3MeCl{\cdot}SO_3K + \frac{1}{3}H_2O$.	Found.
H_2O	2·39	2·44
K (in dry salt) ..	15·95	15·66

Sodium parachlorotoluenesulphonate, $C_6H_3MeCl{\cdot}SO_3Na + H_2O$, crystallised from water in radiate, long, slender needles, and from 10 per cent. alcohol in very long (2—3 cm.) slender needles. It was very soluble in water, and dissolved easily in cold 50 per cent. alcohol. The salt crystallised from 10 per cent. alcohol was analysed :—

0·3968 gram of substance lost 0·0282 gram at 210°, and gave 0·1126 gram Na_2SO_4.

	Calculated for $C_6H_3MeCl{\cdot}SO_3Na + H_2O$.	Found.
H_2O	7·30	7·11
Na (in dry salt) ..	10·07	9·89

The parachlorotoluenesulphonic chloride obtained from these salts was an oil, which was purified by dissolution in light petroleum and subsequent evaporation of the solvent. When cooled in a mixture of ice and salt, it became semi-solid owing to partial crystallisation, and a separation of the crystals from the oil was effected by reverse filtration. The crystals so separated melted for the most part at 5°, and by cooling and filtering several times one-sixth of the chloride was obtained in a form which crystallised in very thin, lustrous scales melting at 18°, and one-third in the form of an oil resembling the chloride prepared from the barium salt "B," the remainder being apparently a mixture of the two.

The sulphonamide obtained from the chloride fusing at 18° crystallised from dilute alcohol in short, lustrous needles melting at 139—140°. It would, therefore, seem to be identical with the 1 : 2 : 4-parachlorotolueneorthosulphonamide described by Heffter (*Annalen*, **221**, 209).

The barium salt "B," crystallising in scales, was converted into the potassium and sodium salts.

Potassium parachlorotoluenesulphonate, $C_6H_3MeCl{\cdot}SO_3K$, crystallised from water in radiate tufts of very small needles. It was more soluble in water than the "A" salt, and nearly always gave supersaturated solutions, which required to be sown with a crystal, and then became a semi-solid, white mass. From 50 per cent. alcohol, in which it was less soluble, it separated in white bundles of short, very slender needles; these, when analysed, gave the following numbers:—

0·3872 gram of substance did not suffer loss at 190°, and gave 0·1368 gram K_2SO_4.

	Calculated for $C_6H_3MeCl{\cdot}SO_3K$.	Found.
K	15·95	15·83

Sodium parachlorotoluenesulphonate, $C_6H_3MeCl{\cdot}SO_3Na + H_2O$, crystallised from water in small scales, and from 50 per cent. alcohol in striated prismatic needles. It was less soluble in water and dilute alcohol than the "A" salt. A specimen crystallised from alcohol was analysed:—

0·4158 gram of substance lost 0·0304 gram at 210°, and gave 0·12 gram Na_2SO_4.

	Calculated for $C_6H_3MeCl{\cdot}SO_3Na + H_2O$.	Found.
H_2O	7·30	7·31
Na (in dry salt)..	10·07	10·08

The parachlorotoluenesulphonic chloride obtained from these salts was an oil which crystallised in a freezing mixture. The corresponding sulphonamide crystallised from dilute alcohol in minute prismatic aggregates melting at about 120°.

The examination of the parachlorotoluenesulphonic acids is being continued with the object of isolating the two isomeric forms in a state of purity; parachlorotoluenesulphonic acids are also being prepared from the isomeric paratoluidinesulphonic acids for the purposes of comparison. There can be little doubt, however, that whatever may be the nature of the "B" salt, the "A" barium salt, which, so far as appearance goes, corresponds with the salt "en petits grains cristallins qui se groupent souvent en mamelons" of Vogt and Henninger (*Ann. Chim. Phys.* [4], **27**, 133), consists, as these chemists believed, of a mixture of two salts. The proportions of the two isomeric salts in this mixed product have yet to be ascertained, but there is reason to believe that the 1 : 2 : 4-salt is present in the smaller quantity; in other words, that the chief product of the action of sulphuric acid on parachlorotoluene is the 1 : 3 : 4-parachlorotoluenemetasulphonic acid.

LXXXIX.—*Action of Iodine on a Mixture of Sulphite and Thiosulphate.*

By Arthur Colefax, M.A., Ph.D., Student of Christ Church, Oxford.

In the course of an investigation of the change proceeding in an acidified solution of sodium thiosulphate (this vol., p. 176), I had occasion to examine the effect produced on adding a solution of iodine to a solution containing both sodium sulphite and sodium thiosulphate. In such a case, iodine might act in one of two ways: either it might give rise to the formation of sodium trithionate, or the iodine might oxidise the sulphite to sulphate, and convert the thiosulphate into tetrathionate. Experiment proved that when the iodine solution was added quickly from a burette, the titration value of the mixture was the sum of the titration values of the components. The same result was obtained with a solution of sodium thiosulphate mixed either with a solution of sodium sulphite, of sodium hydrogen sulphite, or of hydrogen sulphite; also when the iodine acted on hydrogen sulphite and an acidified solution of sodium thiosulphate. In the conclusion of my paper, I said (p. 192): "The addition of iodine to a mixed solution of sodium sulphite and thiosulphate does not produce a trace of sodium trithionate. Hence, Spring's statement is not true of the case where a solution of iodine reacts with a mixed solution of sodium sulphite and thiosulphate."

The above statement attributed to W. Spring, in contradicting which I trust I was in no wise discourteous, though in the interest of truth I may have been too emphatic, I found in the *Ber.*, **7**, 1161: "behandelt man ein Gemenge von schwefeligsaurem Natron und unterschwefeligsaurem Natron mit Jod so wird trithionsaures Natron gebildet."

$$Na_2SO_3 + Na_2S_2O_3 + I_2 = Na_2S_3O_6 + 2NaI.$$

Roscoe and Schorlemmer, in their treatise on Chemistry, have also given the same reference as the source of the above assertion; but it appears that this paper unfortunately is not an authentic communication, but rather an unrevised abstract, and Spring has admitted (*Proc. Chem. Soc.*, No. **111**, 91) that the above equation does not represent the action of iodine on a mixture of sodium sulphite and thiosulphate. The production of trithionate from sulphite and thiosulphate, through the agency of iodine, was, in the original paper, asserted only with reference to potassium salts (compare *Bull. Acad. Roy. Bel.* [2], **38** 112).

To examine further this distinction between potassium and sodium salts which Spring regards as related to the difference in stability of the polythionates of potassium and sodium, the following experiments have been made on the action of iodine on a solution containing both potassium sulphite and thiosulphate.

The method adopted was to determine the value of the iodine titration of the mixed and constituent solutions, and by determining also the acidity developed, to trace the transformations which the sulphite had undergone. When iodine and water oxidise, hydrogen iodide is produced, and consequently there is a development of acidity in the solution. If the ratio between the values of its iodine titration and the developed acidity, as measured by a standard alkali solution be determined for a solution of potassium sulphite, it is possible, from a knowledge of the acidity developed when a solution containing both potassium sulphite and thiosulphate is titrated with iodine, to say what part of that iodine titration value is due to the sulphite present.

The iodine titration value affords a means of ascertaining which of the two following equations represents the action of iodine on a solution containing potassium sulphite and thiosulphate;

$$\text{I. } K_2SO_3 + K_2S_2O_3 + I_2 = I_2 = 2KI + K_2S_3O_6,$$

$$\text{II. } 2K_2S_2O_3 + I_2 = 2KI + K_2S_4O_6, \text{ and } K_2SO_3 + H_2O + I_2 = 2HI + K_2SO_4.$$

The first of these alternatives requires only two-thirds the quantity of iodine necessary for the second, and no acidity is developed.

Before detailing the experiments which have been made, it may be well to notice that Spring in his investigations seemingly used solid iodine, and accordingly its action was slower than when in solution. Again, it was used in quantities in accordance with Equation I, and consequently at the completion of its action, if the action actually occurred as in Equation II, the solution would contain unaltered sulphite and thiosulphate in the presence of tetrathionate.

Action of Iodine on a Solution containing Potassium Sulphite and Thiosulphate.

4·42 grams of potassium thiosulphate were dissolved in 250 c.c. of well boiled water which had been cooled in a current of hydrogen, and 3·8 grams of potassium sulphite were dissolved in the same volume of boiled-out water which had been cooled in an atmosphere of carbon dioxide. The solution of iodine contained 10·16 grams in 1000 c.c. of an aqueous solution of potassium iodide.

10 c.c. of the potassium thiosulphate solution required 10 c.c. of the iodine solution.

10 c.c. of the potassium sulphite solution required 20·8 c.c. of the iodine solution.

The acidity developed after the oxidation of the potassium sulphite solution required 18·30 c.c. of the ammonia solution, using methyl-orange as an indicator.

A mixture consisting of 10 c.c. of each of the above solutions required 30·8 c.c. of the iodine solution before an indication of the presence of excess of iodine was obtained with starch. The developed acidity equalled 18·35 c.c. of the ammonia solution. The blue colour of the starch iodide was discharged by a drop of thiosulphate solution before the addition of the methyl-orange.

In the above experiment, the sulphite and thiosulphate were taken almost in molecular proportion. There had been no action between the potassium salts involving the formation of trithionate; the sulphite had been completely oxidised, and the thiosulphate converted into tetrathionate.

An exactly similar result was obtained when the sulphite was present in excess. 5 c.c. of the potassium thiosulphate and 20 c.c. of the solution of potassium sulphite required 46·55 c.c. of iodine solution, and the developed acidity 36·70 c.c. of the ammonia solution.

A solution of potassium thiosulphate and sulphite, 10 c.c. of each, was titrated with iodine at a temperature near zero. The solutions of sulphite and thiosulphate were cooled to 1°; 10 c.c. of each were withdrawn, and added to partly frozen, boiled-out water.

10 c.c. of the potassium sulphite at 1° required 20·85 c.c. of iodine solution, and the developed acidity equalled 18·40 c.c. of ammonia solution.

The mixed solution required 30·8 c.c. of iodine solution, and the acidity developed equalled 18·35 c.c. of the ammonia solution.

Here again there was no action of the thiosulphate and sulphite.

Iodine does not form, by its action on a dilute solution of sulphite and thiosulphate of potassium, trithionate, but oxidises the sulphite completely to sulphate.

Hence, an equation of the nature

$$M_2SO_3 + M_2S_2O_2 + I_2 = 2MI + M_2S_3O_6$$

does not represent the action of iodine on a mixture of sulphite and thiosulphate, whether of potassium or sodium, under the conditions under which I have worked. The statement of Spring (*Bull. Acad. Roy. Bel.* [2], **38**, 113)—"En résumé l'iode a donc réellement agi sur le mélange du sulfite et de l'hyposulfite, tantôt pour former du tetrathionate, tantôt du sulfate et tantôt du trithionate de potassium, selon que son action se faisait sur l'hyposulfite, sur le sulfite ou sur les deux à la fois," in so far as it represents trithionate of potassium as an immediate product of the interaction of sulphite, thiosulphate, and iodine, is not confirmed by any of the facts which I have observed.

Where the iodine is added in the solid state, its action is slow, particularly if the temperature is kept low. If then a secondary change of the nature $M_2SO_3 + M_2S_4O_6 = M_2S_2O_3 + M_2S_3O_6$ is possible, such an action of the unoxidised sulphite on the tetrathionate will be more likely to occur, when the action of the iodine on a mixture of sulphite and thiosulphate is slow, and when in consequence the sulphite remains in presence of tetrathionate for an appreciable time, Spring has suggested that such a secondary change may account for the formation of trithionate of sodium in a case where he found it amongst the products of the action of iodine on excess of sulphite and thiosulphate of sodium, which had been left to stand for a few days.

I am engaged in investigating the action of sulphites on tetrathionates, and I hope shortly to publish the results of my work. I have found that sulphites do act on tetrathionates, whether of potassium or sodium; thiosulphate being formed in a quantity equivalent to the sulphite which has entered into the reaction.

Potassium trithionate, when formed in the system in which iodine is slowly acting on potassium sulphite and thiosulphate, is the product of the desulphurisation of tetrathionate by sulphite, and is not a result of the union of sulphite with thiosulphate. When the iodine is added quickly from a burette, this secondary change does not take place, and the developed acidity does not decompose the thiosulphate.

A Determination of the Relative Velocities with which Iodine acts on the Sulphite and Thiosulphate occurring together in a Solution.

In attempts to gain knowledge on this point, the following method of experimenting was followed. A solution of sulphite of potassium or sodium is alkaline, but the gradual addition of iodine to such a solution develops acidity, which at a certain point overcomes the alkalinity of the salt, and the solution becomes acid. In titrating a solution of a sulphite with iodine, this point may be ascertained by previously adding to the solution a few drops of methyl-orange. The change in colour of the indicator is not very sharp, but sufficiently so for the purpose of the experiment. The quantity of iodine to be added to overcome the initial alkalinity was determined for a solution of the sulphite, and for a solution of the sulphite mixed with thiosulphate. From these two determinations, the relative velocities with which iodine acts on the sulphite and thiosulphate when they are together in the same solution can be ascertained.

10 c.c. of a solution of sodium sulphite containing 2·85 grams of the salt dissolved in 250 c.c. required 40 c.c. of the iodine solution for complete titration, the developed acidity requiring 36 c.c. of an ammonia solution. A solution of sodium thiosulphate, in 250 c.c. of which there were dissolved 2·505 grams of the salt, required 20 c.c. of the iodine solution for the complete titration of 10 c.c. In equal volumes of the solutions the salts were dissolved in molecular proportion.

10 c.c. of the sulphite solution had an initial alkalinity which was overcome by the acidity developed by the addition of 13·6 c.c. of the iodine solution.

A solution containing 10 c.c. of the sulphite solution together with 10 c.c. of the thiosulphate required 19·2 c.c. of the iodine solution before the developed acidity overcame the alkalinity of the sulphite.

Hence the relative velocities are as

$$\begin{aligned} 13{\cdot}6/40 : 5{\cdot}6/20 &= 0{\cdot}34 : 0{\cdot}28 \\ &= 5 \quad : 4 \quad \text{(approx.)} \end{aligned}$$

up to the point where almost a third of the iodine requisite for complete titration has been added, a quarter of the sulphite initially present is acted on in the same time as one-fifth of the thiosulphate.

For solutions of the potassium salts, in which the sulphite and thiosulphate were also in molecular proportion, the above values for the sulphite and mixed solutions were 14·2 and 20·1 respectively. These values give almost the same ratio, 5 : 4.

This ratio will naturally be subject to the influence of the masses of the sulphite and thiosulphate, and as the titration is more nearly completed, will diminish.

Conclusions.

1. Iodine acts on a solution of sulphite and thiosulphate of potassium or sodium to produce sulphate and tetrathionate. Any trithionate formed is the product of a secondary change between sulphite and tetrathionate.

2. When iodine acts on a solution containing both sulphite and thiosulphate of potassium or sodium present in molecular proportion, it oxidises the sulphite but very little more quickly than it converts the thiosulphate into tetrathionate.

Christ Church Laboratory,
Oxford.

XC.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF EDINBURGH.

No. IX. *The Methyl Salts of Camphoric Acid.*

By JAMES WALKER, D.Sc., Ph.D., F.R.S.E.

MOST of the many formulæ that have been proposed for camphoric acid are based on the assumption that this substance contains two carboxyl groups. Of late, however, Friedel (*Compt. rend.*, **113**, 825) has proposed a formula which represents it as a monocarboxylic acid, the second hydrogen atom which is actually replaceable, being attributed to a hydroxyl group attached to a carbon atom situated between two carbonyl groups. In support of this formula, Friedel brought forward as evidence the existence of two isomeric hydrogen ethyl salts of the acid, one being prepared by direct etherification, the other by half saponification of the diethyl salt. Since the substances as first prepared by Friedel were in the form of oils, and therefore probably not completely free from admixture with each other, it appeared to me of interest to prepare the corresponding methyl compounds, one of which was already known and had been obtained in the crystalline state. Brühl and Braunschweig (*Ber.*, **25**, 1796) and Haller (*Compt. rend.*, **114**, 1516) have since prepared two isomeric hydrogen methyl salts, and have investigated some of their properties. From their experiments, they conclude that Friedel's formula does not represent the true nature of camphoric acid, the two replaceable hydrogen atoms having a similar function in the molecule.

The substances which I have obtained are apparently identical with those described by Brühl and Braunschweig, and by Haller, but as the method of preparation I adopted is to some extent different from those employed by them, and as the investigation of the properties of the compounds was pursued in a somewhat different direction, I may here record the chief of my results. In what follows, I have used the terms *ortho-* and *allo*-methyl hydrogen camphorate employed by Brühl and Braunschweig to distinguish between the two isomerides, although the prefix *ortho-* in this connection seems objectionable on account of the other significations usually attached to it.

Ortho-Methyl Hydrogen Camphorate.

Loir (*Ann. Chim. Phys.* [3], **38**, 483) prepared this substance by distilling a mixture of concentrated sulphuric acid, methyl alcohol, and camphoric acid, replacing the distillate in the flask, and redistilling several times. I repeated Loir's experiments, and after the methyl alcohol had been driven off for the last time, worked up the residue as follows. The contents of the distilling flask were poured into water, and the oil which separated was removed and dissolved in a cold solution of caustic soda, a few drops only remaining unattacked; the solution was then extracted with ether in order to separate the dimethyl camphorate which is formed simultaneously with the hydrogen methyl camphorate. On acidifying the alkaline solution, an oil again separated, and was removed by means of ether. After the ether had been driven off, the oily residue solidified on cooling to a mass of crystals; these were very soluble in ether, much less so in light petroleum, from which they were easily recrystallised. The melting point of the substance after two or three recrystallisations was 76°. Loir states that the substance he obtained melted "environ 68°": it must therefore have been rather impure. The various forms of crystals he describes in his paper were all observed by me at different times, the crystalline habit varying considerably according to the conditions of crystallisation. The *ortho*-methyl hydrogen camphorate of Brühl and Braunschweig has, according to them, the melting point 77—78°; but I was never able, even after repeated recrystallisation of the substance from various solvents, to obtain crystals having a melting point more than a fraction of a degree above 76°. Haller gives 75—76° as the melting point of the purified substance prepared from camphoric acid and methyl alcohol by the action of hydrogen chloride—the method of preparation also adopted by Brühl and Braunschweig.

As hydrogen ethyl salts may often be conveniently prepared from the anhydride of a bibasic acid by boiling it for some time with ethyl alcohol (compare this vol., p. 710), I endeavoured to obtain a hydrogen methyl camphorate by boiling camphoric anhydride with methyl alcohol, but found that, even after prolonged boiling, the anhydride is not appreciably attacked. It then occurred to me that the wished for addition might be effected if sodium methoxide were employed instead of methyl alcohol. As a matter of fact, the reaction takes place with the the greatest readiness, the equation representing it being

$$C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>O + NaO{\cdot}CH_3 = C_8H_{14}<\begin{matrix}COONa\\COOCH_3\end{matrix}.$$

A weighed quantity of sodium is dissolved in methyl alcohol, the solution of sodium methoxide is cooled, and to it is added gradually the calculated quantity of camphoric anhydride (1 mol. to 1 at. sodium). The anhydride should be previously powdered, and the temperature should not be allowed to rise. The reaction takes place with the disengagement of a considerable amount of heat, the anhydride being rapidly attacked, and the sodium methyl camphorate falling out after a time as a white, finely crystalline precipitate. After the mixture has remained for some hours at the ordinary temperature, the methyl alcohol is distilled off, and the solid, pure white residue is dissolved in water, in which it is very soluble. The aqueous solution is acidified, and the oil which separates removed and washed with a little water. After some little time, the oil solidifies to a crystalline mass with a slight syrupy admixture, from which it may be freed by spreading on a porous tile. The residual crystals are dissolved in hot light petroleum and allowed to crystallise. On recrystallisation, the substance showed the same melting point as the hydrogen methyl salt prepared according to Loir's method, namely, 76°.

The following numbers were obtained on analysis:—

0·1541 gram of substance gave 0·3488 gram CO_2 and 0·1180 gram H_2O.

	Calculated for $C_{11}H_{18}O_4$.	Found.
C	61·68	61·66
H	8·41	8·51

0·1193 gram of substance required for neutralisation 5·25 c.c. of 1/9·45 normal baryta solution, phenolphthaleïn being used as indicator.

	Calculated for $C_{11}H_{17}O_4 \cdot H$.	Found.
Replaceable hydrogen......	0·467	0·466

The substance has thus the composition of methyl hydrogen camphorate, and behaves as a monobasic acid. It is easily soluble in alcohol, ether, benzene, chloroform, and carbon bisulphide. It is only slightly soluble in cold light petroleum, but dissolves freely in the boiling solvent. It also readily dissolves in aqueous alkalis or alkaline carbonates. A determination of its solubility in water at the ordinary temperature gave the following numbers:—

100 parts of water at 16° dissolved: I. 0·182 part substance
II. 0·182 " "

In hot water it is considerably more soluble.

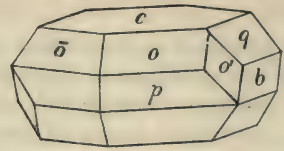
I am indebted to Dr. Hugh Marshall for the following description of the crystals obtained from the petroleum solution:—

"*Ortho-Methyl Hydrogen Camphorate.*

"System.—Rhombic, sphenoidal hemihedral.

"a : b : c = 0·6330 : 1 : 1·2888.

"Forms observed:—$b = \{010\}$, $c = \{001\}$, $o = \kappa\{111\}$, $\bar{o} = \kappa\{1\bar{1}1\}$, $o' = \kappa\{121\}$, $p = \{110\}$, $q = \{011\}$.*



"The large, clear crystals from solution in light petroleum are generally tabular on *c*, occasionally thick prismatic along the a-axis.

"The great majority have a holohedral appearance, as the form *o′* occurs comparatively seldom, and the forms *o* and *ō* are generally, although not always, nearly equally developed. When the form *o′* was observed it was always well marked. In a few cases a different positive sphenoid was represented, one face of which replaced the angle formed by the faces 111, 011, 001. It could not, however, be accurately determined, as its faces were rough and curved. All the other forms, as a rule, gave good reflections."

The dissociation constant of the acid at 25° was determined from the electrolytic conductivity of its aqueous solutions (compare Walker, this vol., p. 696).

Ortho-Methyl Hydrogen Camphorate.

$$\mu_\infty = 350.$$

v.	*μ.*	100*m.*	100*k.*
118	10·54	3·01	0·000794.
236	14·81	4·23	0·000792
472	20·8	5·94	0·000795
944	29·1	8·31	0·000798

K = 0·000795.

The alkaline salts of the acid are very soluble in water, the salts of the alkaline earths fairly so. The copper salt comes down as a bluish-green precipitate when cupric acetate is added to a dilute solution of the sodium salt. This precipitate, although quite insoluble in water, dissolves readily in alcohol, ether, chloroform, and other organic solvents.

The above mode of preparation of the sodium methyl salt from the anhydride seems to be a general method which may be applied to obtain alkyl hydrogen salts of such bibasic acids as form anhydrides, thus,

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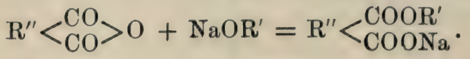
* Professor Osann, who measured the crystals obtained by Brühl and Braunschweig, gives a : b : c = 0·6316 : 1 : 1·2870. The only forms observed were *c*, *p*, *o*, and *ō*. The crystals he investigated were got from aqueous solution.



$$R''\begin{matrix}<CO\\<CO\end{matrix}>O + NaOR' = R''\begin{matrix}<COOR'\\<COONa\end{matrix}.$$

In this way I have prepared various ethyl and methyl hydrogen salts, and have found the products so formed to be identical with those obtained by the methods mentioned in this vol., pp. 709—711. For example, phthalic anhydride unites directly with sodium methoxide in methyl alcohol solution, and the substance obtained, when treated in the manner detailed above, yields hydrogen methyl phthalate melting at 83°. The melting point of the substance obtained from the purified barium salt (this vol., p. 717) is 82·5°.

Dimethyl Camphorate.

This substance may be readily prepared from camphoric anhydride by adding, in addition to the methyl alcohol and sodium used for making sodium methyl camphorate, 1 mol., or rather more, of methyl iodide; the methyl iodide is added when all the camphoric anhydride has been dissolved in the solution of sodium methoxide, and the mixture is then heated in a closed vessel for 24 hours, at 100°. The methyl alcohol, and any excess of methyl iodide, are distilled off, and the residue treated with water. An oil separates which is extracted by agitation with ether, the ethereal solution is dried with calcium chloride, the ether evaporated, and the brownish, oily residue distilled under atmospheric pressure. It passes over almost entirely between 260° and 265°. Brühl and Braunschweig give the boiling point of dimethyl camphorate as 264° under 738 mm. pressure. The refractionated substance (b. p. 262°, uncorr.) is a colourless oil which does not freeze at $-16°$, but becomes very viscid. Its density at 17·5°, compared with that of water at 4° as unity, was found to be 1·075. It is strongly dextrorotatory, the rotation for sodium light, in a tube 200 mm. long, being 103° 56′ at 17°. This corresponds to a specific rotation, $[\alpha]_D = +48{\cdot}32°$. Brühl and Braunschweig found $[\alpha]_D = +48{\cdot}16°$ at 22° to be the specific rotation of dimethyl camphorate. Haller gives $[\alpha]_D = +44{\cdot}40°$.

A combustion gave the following numbers :—

0·1857 gram of substance gave 0·4291 gram CO_2 and 0·1487 gram H_2O.

	Calculated for $C_{12}H_{20}O_4$.	Found.
C	63·16	63·02
H	8·77	8·90

Allo-Methyl Hydrogen Camphorate.

Dimethyl camphorate was half saponified by boiling with the calculated quantity of potash (1 mol. to 1 mol.) in alcoholic solution for 20 minutes. The whole was evaporated down on the water-bath, and water added from time to time until all the methyl alcohol had been driven off: the aqueous solution was then shaken up with ether, to remove the small quantity of unchanged dimethyl camphorate. On acidification, a thick oil separated, which was removed, and a further quantity obtained from the aqueous layer by shaking up with ether. The syrupy liquid obtained after drying the ethereal solution and evaporating, crystallised on standing. The crystalline mass was dissolved in hot light petroleum. At first it crystallised from this solvent in large, apparently quadratic tables, but on recrystallisation it separated in clusters of short, thick needles. These had the melting point 85·5°, which was not appreciably altered on repeated recrystallisation. Brühl and Braunschweig give 86—87° as the melting point of the allo-methyl hydrogen camphorate prepared by the half saponification of ortho-ethyl allo-methyl camphorate. Haller gives 85—86° for the compound he obtained.

The following numbers were obtained on analysis :—

0·2028 gram of substance gave 0·4596 gram CO_2 and 0·1566 gram H_2O.

	Calculated for $C_{11}H_{18}O_4$.	Found.
C	61·68	61·81
H	8·41	8·58

The substance very closely resembles the isomeric acid ethereal salt in its solubility relations. It dissolves readily in alcohol, ether, benzene, chloroform, carbon bisulphide, and acetone. In hot light petroleum, it dissolves easily, but is only slightly soluble in the cold solvent. In water it is less soluble than its isomeride, as the following numbers show :—

100 parts of water at 16° dissolved—I. 0·114 part substance.
II. 0·116 „ „

The quantity of the ortho-methyl compound dissolved by the same amount of water is 0·182 part.

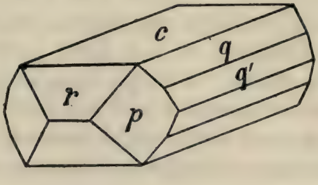
Brühl and Braunschweig were unable to cultivate crystals with faces suitable for measurements of angle. I experienced the same difficulty when the usual solvents were employed, but by using a solvent of low vapour pressure at the ordinary temperature, so that the evaporation proceeded very slowly, I obtained well developed crystals with bright plane faces. I have again to thank Dr. Marshall for the following account of the crystals obtained by crystallisation from metaxylene :—

"*Allo-Methyl Hydrogen Camphorate.*

"System.—Rhombic, sphenoidal hemihedral.

"$a : b : c = 0·9727 : 1 : 1·2781$.

"Forms observed:—$c = \{001\}$, $p = \{110\}$, $q = \{011\}$, $q' = \{021\}$, $r = \{101\}$.



"The substance is necessarily hemihedral, as it is optically active; but as only prism and end faces are present, there is no indication of hemihedry in the outward form.

"The crystals are colourless and transparent, and vary greatly in habit. One of the most frequent conditions is that shown. From solutions in carbon bisulphide and light petroleum large tabular crystals are sometimes obtained, consisting only of the forms *c* and *p*. These have a quadratic appearance, as the prism angle is nearly 90°. Solutions in acetone give crystals roughly resembling a combination of the cube and octahedron, composed of the forms *p*, *q*, *r*, and *c*. Even with the same solvent, considerable variations are exhibited. Sometimes *c* is small, and the crystals become prismatic along the a-axis. There is an indistinct cleavage parallel to 021."

A determination of the dissociation constant at 25° gave the following results:—

Allo-Methyl Hydrogen Camphorate.

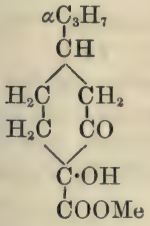
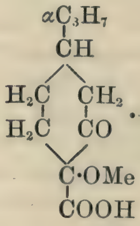
$\mu_\infty = 350.$

v.	μ.	$100m$.	$100k$.
209·5	16·24	4·64	0·00108
419·0	22·8	6·51	0·00108
838·0	31·5	9·00	0·00106

K = 0·00108.

The salts of the acid, so far as they were examined, behaved precisely like those of the isomeride. In particular, the copper salt was found to be insoluble in water, but easily soluble in the usual organic solvents.

It was specially with a view to determine the dissociation constants of the isomeric methyl hydrogen camphorates that I undertook their preparation, for it seemed to me that, from a knowledge of these magnitudes, it would be possible to decide conclusively if Friedel's formula for camphoric acid truly represented its constitution. According to Friedel, the two isomeric substances correspond to the two formulæ—

I.  , and II.  .

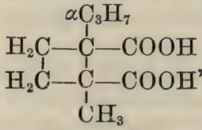
Now Ostwald's researches enable us to predict what relation should subsist between the constants of these substances, and of the camphoric acid from which they are derived. The dissociation constant of camphoric acid, as determined by Ostwald, is 0·00225 (*Zeit. physikal. Chem.*, **3**, 402). Formula I belongs to a substance whose only replaceable hydrogen atom is in a hydroxyl group attached to a tertiary carbon atom. Such a substance could scarcely have a dissociation constant greater than the tenth part of that pertaining to camphoric acid itself (compare Bader, *Zeit. physikal. Chem.*, **6**, 290). The isomeride, on the other hand, ought to have a constant greater than that of camphoric acid, for in the analogous case of methoxyacetic acid, K = 0·0335, the constant is greater than that of the hydroxy-acid, glycollic acid, K = 0·0228, from which it is derived (Ostwald, *loc. cit.*, 183—184). If Friedel, then, is correct in assuming that camphoric acid contains only one carboxyl group, the constants of the two isomeric methyl hydrogen salts should be widely different, and of the order $<$ 0·0002 and $>$ 0·003 respectively. As a matter of fact, we find that the two constants are not far from being equal, viz., 0·00079 and 0·00108. These values, too, agree very well with the assumption that camphoric acid is a dicarboxylic acid. I have shown (this vol., p. 715) that the value of the constant of a dicarboxylic acid is to that of the monethyl ether derived from it in the ratio of 2·3 : 1, this being the mean value for ten weak and moderately strong acids. The corresponding ratio is somewhat less for the monomethyl ethereal salts, the following being the numbers as yet actually obtained (*loc. cit.*, 717) :—

	Ratio.
Succinic acid	2·1 : 1
Phthalic acid	1·8 : 1
Tartaric acid	2·1 : 1[*]

Using Ostwald's value for camphoric acid, we obtain the following ratios for the methyl hydrogen salts :—

	Ratio.
Ortho-methyl hydrogen camphorate	2·1 : 1
Allo-methyl hydrogen camphorate	2·8 : 1

The agreement is as close as could be expected. With Friedel's formula the ratios should be $> 10 : 1$ and $< 0·7 : 1$.

The conclusion, then, to which a discussion of the dissociation constants leads is that arrived at on other grounds by Brühl and Braunschweig, and by Haller. Brühl, however, goes further, and attributes to camphoric acid the formula given by Victor Meyer and Ballo, namely, 

$$\begin{array}{l} \qquad\;\; \alpha C_3H_7 \\ \qquad\quad | \\ H_2C-C-COOH \\ \;\;\;\;| \qquad | \\ H_2C-C-COOH \\ \qquad\quad | \\ \qquad\;\; CH_3 \end{array},$$

according to which it is a succinic acid derivative. Ostwald pointed out that this formula is highly improbable, because the dissociation constant of the acid is only a third of that of succinic acid, whereas all the hydrogen and carbon acids derived from that substance have constants greater than that of the parent acid. The mere fact of there being a tetramethylene ring in the structure is not sufficient to account for the smallness of the constant (compare this vol., p. 705). There would rather seem to be some peculiarity in the constitution of camphor derivatives which depresses the value of the constant, not only of camphoric acid, but of the other related carboxyl acids. Thus camphorcarboxylic acid, campholic acid, and the hydrogen methyl camphorates have all values much lower than we should be disposed *a priori* to attribute to them, on the assumption that they are carboxyl acids of the ordinary open or closed chain type.

[*] Walden, *Zeit. physikal. Chem.*, **8**, 474.

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ERRATA.

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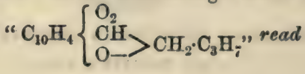
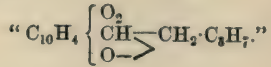
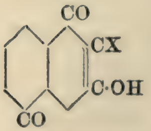
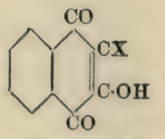
Page	Line	
390	11*	*for* "$C_{33}H_{45}NO_{11},HAuCl_4$" *read* "$C_{33}H_{45}NO_{12},HAuCl_4$."
391	3	,, "$C_{32}H_{45}NO_{11}$" *read* "$C_{33}H_{45}NO_{12}$."
531	16	,, "thiocarbamides" *read* "thiocarbimides."
,,	18	,, "thiocarbamide" *read* "thiocarbimide."
568	3*	foot-note, *for* "and found from his" *read* "and found that his."
570	9	*for* "metadichlorobromoquinone" *read* "metadichlorodibromoquinone."
614	25	,, "bromide" *read* "bromine."
617		foot-note, in the last two symbols replace the double lines in the vertical sides of the hexagons by single lines.
618	11*	replace the "OH" at the bottom angle of the hexagon by "CO."
619	7*	foot-note, *for* " $C_{10}H_4\left\{\begin{array}{l}O_2\\CH\\O-\end{array}\right. > CH_2\cdot C_3H_7$" *read* " $C_{10}H_4\left\{\begin{array}{l}O_2\\CH-\\O-\end{array}\right. > CH_2\cdot C_3H_7$."
621		bottom line, foot-note, *for* "" *read* "."
625	8	at bottom of hexagon, *for* "$CO\cdot O\cdot C_2H_3O$" *read* "$C\cdot O\cdot C_2H_3O$."
631	17	*for* "sp. gr. 1·10" *read* "sp. gr. 1·20."
638	14	*omit* "(Paternò)."
639 646 647		In all the formulæ *for* "α_1" *read* "α."
684	11	*for* "mercuric zinc cyanide" *read* "mercuric potassium cyanide."
912	18*	,, "determined by crystallisation" *read* "determined by cupellation."

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* From bottom.

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